K
505
L84E
v.4

Foundation Che

Gurukul Kangri

Digitized by Arya Samaj Foundation Chennai and eGangotri

07 7823

गुरुकुल कांगड़ी विश्वविद्यालय, हरिद्वार
पुस्तकालय

विषय संख्या R 505
पुस्तक संख्या L94E V.24
आगत पंजिका संख्या 69444

पुस्तक पर किसी प्रकार का निशान लगाना वर्जित है। कृपया १५ दिन से अधिक समय तक पुस्तक अपने पास न रखें।

पुस्तकालय, गुरुकुल कांगड़ी विश्वविद्यालय
हरिद्वार।

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

R
E25
L84E
V.24

COMPILED

पुस्तकालय
गुरुकुल कांगड़ी विश्वविद्यालय, हरिद्वार

पुस्तक-वितरण की तिथि नीचे अंकित है।

इस तिथि सहित १५वें दिन तक यह पुस्तक पुस्तकालय में वापिस आ जानी चाहिए। अन्यथा ५ पैसे प्रतिदिन के हिसाब से विलम्ब-दण्ड लगेगा।

STOCK VERIFICATION
Central
Library
2024-25 G.K.U.

STOCK VERIFICATION
Central
Library
2024-25 G.K.U.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

63444

COMPILED

077823

स्तक प्रमाणीकरण १९८४-१९८५

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

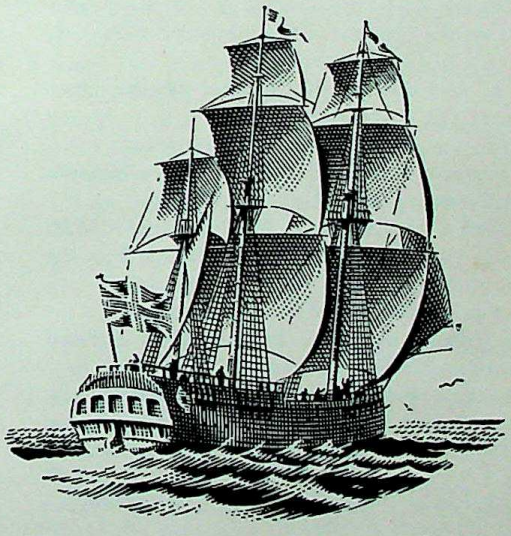
Digitized by Arya Samaj Foundation Chennai and eGangotri

63444

COMPILED

CHECKED 1973
Initial ....

077823



ENDEAVOUR

A review of the progress of science, published in five languages

VOLUME XXIV : 1965

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Author index

Digitized by Arya Samaj Foundation Chennai and eGangotri

AMBROSE, E. J. Cell movements. 27.
BIONDI, M. A. Recombination of ions and electrons. 40.
BLACK, M. Coccoliths. 131.
BRACHET, J. L. A. Acetabularia. 155.
CLOWES, F. A. L. Meristems and the effect of radiation on cells. 8.
COLBURN, C. B. The fluorides of nitrogen. 138.
DAVID, P. M. The surface fauna of the ocean. 95.
DOLLFUS, A. The planets. 87.
DOWDEN, D. A. Heterogeneous catalysis. 69.
EASTHAM, J. F. *See* WILLIAMS, F. C. and EASTHAM, J. F.
EDITORIAL
Centenary of Mendelism. 2.
Educating the young scientist. 62.
The International Biological Programme. 118.
FLEMING, M. G. and KITCHENER, J. A. Development of the theory of the flotation of sulphide ores. 101.
HARRIS, H. The ribonucleic acids in the nucleus and cytoplasm of animal cells. 50.
JOHNSON, A. W. Polyacetylenic compounds in nature. 126.
KITCHENER, J. A. *See* FLEMING, M. G. and KITCHENER, J. A.
KOMPFNER, R. The development of the travelling wave tube. 106.
LEVI SETTI, R. Hypernuclei. 119.
MERRIFIELD, R. B. Solid-phase peptide syntheses. 3.
MILLER, A. J. Road traffic flow: some theories and their applications. 143.
MORTON, R. A. Quinones as biological catalysts. 81.
ROTHERHAM, L. The brittle fracture of steel. 45.
ROTHSCHILD, M. The rabbit flea and hormones. 162.
SALISBURY, F. B. The initiation of flowering. 74.
SARJEANT, W. A. S. The Xanthidia. 33.
UBBELOHDE, A. R. The anisotropy of graphite. 63.
WIGGLESWORTH, SIR VINCENT B. Insect hormones. 21.
WILLIAMS, F. C. and EASTHAM, J. F. The search for a variable-speed induction motor. 149.
YOUNG, J. Z. Two memory stores in one brain. 13.

Book reviews

ABETTI, G. and HACK, M. Nebulae and Galaxies (translated from the Italian by V. Barocas). 111.
ALFREY, G. F. Physical Electronics. 169.
ALIMARIN, I. P. and PETRIKOVA, M. N. Inorganic Ultramicroanalysis (translated from the Russian by M. G. Hell). 112.
Annual Reports on the Progress of Chemistry for 1963, Vol. LX. 169.
BARLOW, R. B. Introduction to Chemical Pharmacology (second edition). 116.
BARRINGTON, E. J. W. Hormones and Evolution. 113.
BELCHER, R., WILSON, C. L., and WEST, T. S. New Methods of Analytical Chemistry (second edition). 170.
BHACCA, N. S. and WILLIAMS, D. H. Applications of N.M.R. Spectroscopy in Organic Chemistry; Illustrations from the Steroid Field. 171.
BIRSS, ROBERT R. Symmetry and Magnetism. 169.
BISHOP, C. and SURGENOR, D. M. (Editors). The Red Blood Cell, a Comprehensive Treatise. 172.
BONNER, J. and TS'O, P. (Editors). The Nucleohistones. 114.
BOYLAND, E. (Editor). Mechanisms of Carcinogenesis: Chemical, Physical and Viral. British Medical Bulletin, Vol. XX, No. 2. 59.
BRODAL, A. and FÄNGE, R. (Editors). The Biology of Myxine. 174.
BROOK, ALAN J. The Living Plant. 115.
BUDZIKIEWICZ, H., DJERASSI, C., and WILLIAMS, D. H. Interpretation of Mass Spectra of Organic Compounds. 57. Structure Elucidation of Natural Products by Mass Spectrometry. Vol. I, Alkaloids. 113.
CALDIN, E. F. Fast Reactions in Solution. 112.
CARRICK, R., HOLDGATE, M., and PRÉVOST, J. (Editors). Biologie antarctique. 172.
CHIU, HONG-YEE and HOFFMANN, WILLIAM F. (Editors). Gravitation and Relativity. 56.
CHORLEY, R. J., DUNN, A. J., and BECKINSALE, R. P. The History of the Study of Landforms *or* The Development of Geomorphology, Vol. I: Geomorphology before Davis. 176.
CLARK, R. B. Dynamics in Metazoan Evolution: the Origin of the Coelom and Segments. 173.
COONEY, D. G. and EMERSON, R. Thermophilic Fungi, an Account of their Biology, Activities, and Classification. 174.
COTTRELL, A. H. The Mechanical Properties of Matter. 56.
CUTTING, WINDSOR C. (Editor). Annual Review of Pharmacology, Vol. IV. 115.
DAMASK, A. C. and DIENES, G. J. Point Defects in Metals. 58.
DANILEVSKII, A. S. Photoperiodism and Seasonal Development of Insects (translated from the Russian by J. Johnston). 172.
DOGIEL, V. A. General Parasitology (translated from the Russian by Z. Kabata). 172.
DUCHESNE, J. (Editor). The Structure and Properties of Biomolecules and Biological Systems. 172.
EDWARDS, JOHN O. Inorganic Reaction Mechanisms: An Introduction. 112.
FALK, J. E. Porphyrins and Metalloporphyrins, Vol. II. 58.
GATOS, HARRY C. (Editor). Surface Science, Vol. I, no. 1, January 1964. 57.
GELL-MANN, M. and NE'EMAN, Y. The Eightfold Way. 168.
GERSHENSON, D. E. and GREENBERG, D. A. Anaxagoras and the Birth of Physics. 116.
GOLD, V. (Editor). Advances in Physical Organic Chemistry, Vol. II. 57.
GOWING, MARGARET. Britain and Atomic Energy 1939–1945. 176.
HADDOW, A. and WEINHOUSE, S. (Editors). Advances in Cancer Research, Vol. VIII. 175.
HALL, MARIE BOAS (Editor). Experiments and Considerations touching Colours, by Robert Boyle. 60.
HARLAND, W. B., SMITH, A. GILBERT, and WILCOCK, B. (Editors). The Phanerozoic Time-scale. 171.
HAYES, WILLIAM. The Genetics of Bacteria and their Viruses; Studies in Basic Genetics and Molecular Biology. 59.
HOSKIN, M. A. William Herschel and the Construction of the Heavens. 60.
HUMMEL, DIETER. Identification and Analysis of Surface-active Agents by Infrared and Chemical Methods, Text Volume and Spectra Volume (translated from the German by E. A. Wulkow). 170.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

JAMES, A. T. and MORRIS, L. J. (Editors). New Biochemical Separations. 114.

Digitized by Arya Samaj Foundation Chennai and eGangotri

JERRARD, H. G. and MCNEILL, D. B. A Dictionary of Scientific Units, including Dimensionless Numbers and Scales. 56.

KARLING, JOHN S. Synchytrium. 115.

KING-HELE, DESMOND. Theory of Satellite Orbits in an Atmosphere. 171.

KONDRAT'EV, V. N. Chemical Kinetics of Gas Reactions (translated from the Russian by J. M. Crabtree and S. N. Carruthers; edited by N. B. Slater). 57.

KRIVOGLAZ, M. A. and SMIRNOV, A. The Theory of Order-Disorder in Alloys (translated from the Russian by Scripta Technica, and edited by B. Chalmers). 176.

LANDY, M. and BRAUN, W. (Editors). Bacterial Endotoxins. 173.

LAURENCE, D. R. and BACHARACH, A. L. (Editors). Evaluation of Drug Activities: Pharmacometrics, Vols. I and II. 175.

LECLERCQ, R. Traité de la méthode scientifique. 111.

LEHNINGER, ALBERT L. The Mitochondrion, Molecular Basis of Structure and Function. 113.

LEOPOLD, L. B., WOLMAN, M. GORDON, and MILLER, J. P. Fluvial Processes in Geomorphology. 58.

LINSKENS, H. F. (Editor). Pollen Physiology and Fertilization. 174.

LOCKE, MICHAEL (Editor). Cellular Membranes in Development. 114.

LOCKWOOD, A. P. M. Animal Body Fluids and their Regulation. 60.

MARK, H. F., GAYLORD, N. G., and BIKALES, N. M. (Editors). Encyclopedia of Polymer Science and Technology: Plastics, Resins, Rubbers, Fibers. Vol. I, A—Amino Acids. 113.

MARKSTEIN, GEORGE H. (Editor). Nonsteady Flame Propagation. 111.

MCMILLAN, P. W. Glass-Ceramics. 175.

MITCHELL, H. H. Comparative Nutrition of Man and Domestic Animals, Vols. I and II. 175.

MOORHOUSE, R. G. (Editor). Strong Interactions and High Energy Physics. 111.

MORSE, PHILIP M. Thermal Physics (third edition). 111.

MURRELL, J. N. The Theory of the Electronic Spectra of Organic Molecules. 170.

NESS, H. C. VAN. Classical Thermodynamics of Non-electrolyte Solutions. 169.

O'BRIEN, R. D. and WOLFE, L. S. Radiation, Radioactivity, and Insects. 59.

O'DWYER, J. J. The Theory of Dielectric Breakdown of Solids. 112.

OURISSON, G., CRABBÉ, P., and RODIG, O. R. Tetracyclic Triterpenes. 170.

PAOLETTI, R. and KRITCHEVSKY, D. (Editors). Advances in Lipid Research, Vols. I and II. 173.

PARTINGTON, J. R. A History of Chemistry, Vol. IV. 116.

PORTER, K. R. and BONNEVILLE, M. A. An Introduction to the Fine Structure of Cells and Tissues (second edition). 169.

RAO, C. N. R. Chemical Applications of Infrared Spectroscopy. 57.

RICHARDS, J. H. and HENDRICKSON, J. B. The Biosynthesis of Steroids, Terpenes, and Acetogenins. 171.

RICHARDSON, J. A. Physics in Botany. 115.

ROUILLER, CH. (Editor). The Liver: Morphology, Biochemistry, Physiology, Vols. I and II. 174.

RUTHERFORD, D. E. Introduction to Lattice Theory. 168.

SAVORY, THEODORE. Arachnida. 174.

SCHWARZ, J. C. P. (Editor). Physical Methods in Organic Chemistry. 58.

SIEGEL, B. M. (Editor). Modern Developments in Electron Microscopy. 112.

STARY, J. The Solvent Extraction of Metal Chelates. 170.

STREHLER, B. L. (Editor). Advances in Gerontological Research, Vol. I. 173.

TAVOLGA, WILLIAM N. (Editor). Marine Bio-Acoustics. 59.

WILBUR, K. M. and YONGE, C. M. (Editors). Physiology of Mollusca, Vol. I. 60.

WILLIAMS, WATKIN. Genetical Principles and Plant Breeding. 115.

WISE, EDMUND M. (Editor). Gold; Recovery, Properties, and Applications. 176.

YOUNG, J. Z. A Model of the Brain. 173.

ZARROW, M. X., YOCHIM, J. M., MCCARTHY, J. L., and SANBORN, R. C. Experimental Endocrinology, a Sourcebook of Basic Techniques. 114.

Subject index

The articles are arranged, with regard to subjects, in numerical order according to the Universal Decimal Classification (Brit. Std. 1000). An alphabetical key is to be found on page IV.

37 Education

378.3:53/59 Educating the young scientist (Editorial). 62.

5 General Science

53/59:378.3 Educating the young scientist (Editorial). 62.

519 Applied Statistics

519.24:656.021 Road traffic flow: some theories and their applications. Miller, A. J. 143.

52 Astronomy

523.4 The planets. Dollfus, A. 87.

53 Physics

539.126.6 Hypernuclei. Levi Setti, R. 119.

539.184.3 Recombination of ions and electrons. Biondi, M. A. 40.

539.56:669.14 The brittle fracture of steel. Rotherham, L. 45.

54 Chemistry

541.128.13 Heterogeneous catalysis. Dowden, D. A. 69.

546.17.16 The fluorides of nitrogen. Colburn, C. B. 138.

546.26–1:622.336 :548.55 The anisotropy of graphite. Ubbelohde, A. R. 63.

547.314 :581.192.2 Polyacetylenic compounds in nature. Johnson, A. W. 126.

547.466.1:577.1 Solid-phase peptide syntheses. Merrifield, R. B. 3.

547.567 Quinones as biological catalysts. Morton, R. A. 81.

547.963.32 :576.311.1 :577.1 The ribonucleic acids in the nucleus and cytoplasm of animal cells. Harris, H. 50.

548 Crystallography

548.55:546.26–1 :622.336 The anisotropy of graphite. Ubbelohde, A. R. 63.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

56 Palaeontology

561.26:582.263 Coccoliths. Black, M. 131.

561.27 The Xanthidia. Sarjeant, W. A. S. 33.

57 Biological Sciences. Biochemistry

574.6 (100) The International Biological Programme (Editorial). 118.

575.11:92 Centenary of Mendelism (Editorial). 2.

576.311.1:577.1:547.963.32 The ribonucleic acids in the nucleus and cytoplasm of animal cells. Harris, H. 50.

576.33:581.17.035 Meristems and the effect of radiation on cells. Clowes, F. A. L. 8.

576.4 Cell movements. Ambrose, E. J. 27.

577.1:547.466.1 Solid-phase peptide syntheses. Merrifield, R. B. 3.

577.1:547.963.32:576.311.1 The ribonucleic acids in the nucleus and cytoplasm of animal cells. Harris, H. 50.

577.18:595.7 Insect hormones. Wigglesworth, Sir Vincent B. 21.

58 Botany

581.145.1 The initiation of flowering. Salisbury, F. B. 74.

581.17.035:576.33 Meristems and the effect of radiation on cells. Clowes, F. A. L. 8.

581.192.2:547.314 Polyacetylenic compounds in nature. Johnson, A. W. 126.

582.263 Acetabularia. Brachet, J. L. A. 155.

582.263:561.26 Coccoliths. Black, M. 131.

59 Zoology

591.134:595.775 The rabbit flea and hormones. Rothschild, M. 162.

591.481.1:594.56 Two memory stores in one brain. Young, J. Z. 13.

591.9 (26.01) The surface fauna of the ocean. David, P. M. 95.

594.56:591.481.1 Two memory stores in one brain. Young, J. Z. 13.

595.7:577.18 Insect hormones. Wigglesworth, Sir Vincent B. 21.

595.775:591.134 The rabbit flea and hormones. Rothschild, M. 162.

621.3 Electrical Engineering

621.313.333 The search for a variable-speed induction motor. Williams, F. C. and Eastham, J. F. 149.

621.385.63 The development of the travelling wave tube. Kompfner, R. 106.

622 Minerals

622.336:548.55:546.26–1 The anisotropy of graphite. Ubbelohde, A. R. 63.

622.366:622.765 Development of the theory of the flotation of sulphide ores. Fleming, M. G. and Kitchener, J. A. 101.

622.765:622.366 *Idem.*

65 Communication

656.021:519.24 Road traffic flow: some theories and their applications. Miller, A. J. 143.

669 Metallurgy

669.14:539.56 The brittle fracture of steel. Rotherham, L. 45.

9 History of Science. Biography

92:575.11 Centenary of Mendelism (Editorial). 2

Alphabetical key

Acetabularia 582.263
Animal maturation 591.134
Anisotropy 548.55
Astronomy 52
Biochemistry 577.1
Biography 92
Botany 58
Brain 591.481.1
Brittle fracture 539.56
Cell movements 576.4
Chemistry 54
Coccoliths 561.26
Communications 65
Crystallography 548
Cytology 576.3
Cytoplasm movement 576.4
Education 378
Electrical engineering 621.3
Electronics 621.38
Flotation of ores 622.765
Flowering, initiation of 581.145.1
Graphite 546.26
Green algae 582.26
Heterogeneous catalysis 541.128.13
Hormones 577.18
Hypernuclei 539.126.6
Induction motors 621.313.333
Insects 595.7
International Biological Programme 574.6
Mendelism 575.11
Meristems 581.17.035
Metallurgy 669
Minerals 622
Nitrogen fluorides 546.17.16
Nucleic acids 547.963
Ocean surface fauna 591.9
Octopus, memory of 594.56
Palaeobotany 561
Palaeontology 56
Peptides 547.466.1
Physical chemistry 541.1
Physics 53
Planets 523.4
Plant chemistry 581.19
Polyacetylenic compounds 547.314
Quinones 547.567
Rabbit flea 595.775
Recombination of ions and electrons 539.184.3
RNA 547.963.32
Steel 669.14
Traffic flow 656.021
Travelling wave tubes 621.385.63
Xanthidia 561.27
Zoology 59

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Printed by The Kynoch Press, Birmingham 6
for the publishers, Imperial Chemical Industries Limited, London, S.W.1

91

ENDEAVOUR

VOLUME XXIV JANUARY 1965

Digitized by Ary

A review of the progress of science, published in five languages

Editor TREVOR I. WILLIAMS, M.A., B.Sc., D.Phil., F.R.I.C.
Foreign Editor G. N. J. BECK, B.Sc., A.M.I.E.E.
Assistant Editor W. A. OSMAN, B.Sc., M.Sc., A.R.C.S.

Contents

575.11:92
2 Editorial: Centenary of Mendelism

547.466.1:577.1
3 Solid-phase peptide syntheses
R. B. Merrifield, B.A., Ph.D.

581.17.035:576.33
8 Meristems and the effect of radiation on cells
F. A. L. Clowes, M.A., D.Phil.

591.481.1:594.56
13 Two memory stores in one brain
J. Z. Young, M.A., F.R.S.

577.18:595.7
21 Insect hormones
Sir Vincent B. Wigglesworth, C.B.E., M.D., F.R.S.

576.4
27 Cell movements
E. J. Ambrose, M.A., D.Sc.

561.27
33 The Xanthidia
William A. S. Sarjeant, B.Sc., Ph.D., F.G.S.

539.184.3
40 Recombination of ions and electrons
Manfred A. Biondi, B.S., Ph.D.

539.56:669.14
45 The brittle fracture of steel
L. Rotherham, D.Sc., F.R.S.

547.963.32:576.311.1:577.1
50 The ribonucleic acids in the nucleus and cytoplasm of animal cells
Henry Harris, B.A., M.B., B.S. (Syd), M.A., D.Phil. (Oxon)

56 Book reviews

Some books received (cover iii)

Communications to the Editor should be addressed to Endeavour, South Block, Thames House, Millbank, London S.W.1 Telephone: Tate Gallery 2181

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Centenary of Mendelism

Digitized by Arya Samaj Foundation Chennai and eGangotri

In 1865, Gregor Johann Mendel (1822–1884) read his paper '*Versuche über Pflanzenhybriden*' to an unappreciative audience of the *Naturforschender Verein* in Brno. The following year, it appeared in print in the Society's *Verhandlungen*, but again failed to attract attention. Mendel gained no recognition in his lifetime, for it was not until 1900 that H. de Vries and others rediscovered his work, and ensured worldwide acknowledgment of its importance.

To Mendel indisputably goes the credit for formulating a theory of inheritance that would stand the test of both qualitative and quantitative experiment, but it must not be forgotten that others who fell short of success had already travelled some considerable way towards it. Linnaeus (1707–1778) believed that new plant species arise by natural hybridization. The German botanist Joseph Gottlieb Koelreuter (1733–1806) put it to the test of experiment. In the 1760s and 1770s he made over 500 different crosses and raised first and second generation (F1 and F2) hybrids, and back-crossed and compound hybrids. The results put him in a unique position to pronounce upon the issue of plant sexuality and to answer the vexed question of the role of the sexes in reproduction. Unfortunately, most of his work appeared in a little-known book (*Vorläufige Nachricht von einigen das Geschlecht der Pflanzen betreffenden Versuchen* . . . Leipzig, 1761–1766), where it lay forgotten for over half a century. It contains graphic descriptions of his discoveries—the wonderful uniformity of all the F1 hybrids in every cross he attempted; the identity of all his reciprocal crosses; and the variability and tendency to reversion of his F2 and back-crossed hybrids. Koelreuter concluded that both sexes contribute equally to the formation of the offspring, and that since hybrids revert sooner or later to the parental species, they cannot form fresh species.

Koelreuter pictured fertilization as a sort of chemical reaction between two germinal fluids. This rather naive chemical imagery was discarded by Carl Gaertner (1772–1850), who in the 1830s and 1840s repeated and extended many of Koelreuter's experiments. In 1849, he published an account of his 10 000 experiments, together with copious references to the work of others, in his book *Versuche und Beobachtungen über die Bastarderzeugung im Pflanzenreich* (Stuttgart, 1849). For the reader of German —and Mendel seems to have read exclusively German works—Gaertner made available all the important early genetical work. Also he attempted, in a less superficial way than Koelreuter, to search for the laws governing the resemblance of hybrids to their parents. This led him not only to introduce useful terms such as 'factor' and 'element' but to realize that no single law governs the expression of parental characters in F1 hybrids. They are not all intermediate, as Koelreuter held, but manifest a great range from exact intermediacy to almost complete identity with one of the parental species.

The French botanist Charles Naudin (1815–1899) approached closer than anyone else to the Mendelian concept of germinal segregation. His interest in hybridization was chiefly that of a taxonomist, but he was struck by the fact that some of his hybrids showed complete reversion to the two parental species in the F2 generation. He attributed this to the '*disjonction des essences spécifiques* in the formation of pollen and ovules. Having accepted G. B. Amici's assertion of 1830 that fertilization involves the fusion of the contents of one pollen grain with one ovule, he was able to go on to consider the results of random fertilizations between pollen grains and ovules '*disjoints dans le sens du père et dans le sens de la mère*', and he showed that they agreed with some of his experiments. Naudin put forward this hypothesis in 1856, but he did not state it fully, with the experimental backing, until 1865. Although widely discussed, it won little support either in France or in England; it seems to have been unknown in Germany.

In Gaertner's book of 1849, however, Mendel would have found the details of all the early experiments in the crossing of varieties of the edible pea (*Pisum sativum*). Such crosses had been made by Thomas Andrew Knight (1759–1838) in the 1780s, and by John Goss (1787–1833) and Alexander Seton (fl. c. 1810–1835) in the 1820s. They all noted that such contrasted characters as yellow and green cotyledon colour were never blended in the cross-bred seeds. Instead, all the F1 seeds were either one colour or the other. The F2 seeds, on the other hand, were yellow and green mixed apparently indiscriminately. These observations were clear examples of Mendelian dominance and segregation, but for Knight, Seton, and Goss they were incidental to the main purpose of their experiments. In Knight's case this was to see whether two kinds of pollen can act together on the same ovule and on the same ovary, and in the case of Goss and Seton, to test the supposed direct colour action of foreign pollen on the seed coats.

Mendel began his experiments in the crossing of peas in 1856, not with the intention of testing the direct action of foreign pollen or to see if two kinds of pollen can act together, but to discover the connection between hybridization and the history of the evolution of organic forms.

All Mendel's predecessors counted seeds on occasions, but it never occurred to them that if they grew all the hybrids which they produced from a given cross and counted all the seeds in all the fruits yielded by these hybrids they might make an important discovery. Mendel did realize this, and we can attribute his awareness to three causes. Firstly, he knew from the work of his predecessors how hybrids behave. Secondly, he knew from his student days in Vienna of the cytological discoveries in the 1850s relating to the process of fertilization which completely supported Amici's assertion of 1830. Thirdly, he had also studied mathematical physics in Vienna, and thus had realized the value of statistical methods in studying apparently disorderly phenomena. The result was that for the F2 hybrids for which Koelreuter and Gaertner found no law of inheritance, Mendel found a statistical law.

Mendel's classic paper gave, for the first time, an analysis of heredity made by treating each characteristic separately and following the hereditary transmission of each from one generation to the next. There is no mention of specific essences or specific building forces; instead, the characteristics of the offspring are attributed to elements in the cell. Mendel showed, with convincing evidence, how the behaviour of hybrids can be explained in terms of the transmission, segregation, and recombination of these hereditary elements.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Solid-phase peptide syntheses

Digitized by Arya Samaj Foundation Chennai and eGangotri

R. B. Merrifield

Many important biochemical questions, such as the mechanisms of hormone and enzyme action, might be solved if the complex proteins and polypeptides involved could be synthesized. Unfortunately, the classical methods are tedious and often give low yields. This article describes a rapid and simplified process in which the peptide is held in the solid phase during all the intermediary stages of synthesis. The process may also be applicable to the synthesis of polynucleotides.

One of the significant problems still challenging the chemist is the synthesis of polypeptides and proteins—many important questions in chemistry and biology depend for answers on our ability to make these compounds. Perhaps the most straightforward examples of the uses of synthesis are the classical proofs of the structures of naturally occurring compounds. More interesting, however, are the broader questions involving the relation of chemical structure to biological activity. How does a hormone function, and how can its action be regulated or modified? Why are enzymes such potent and specific catalysts? What is the mechanism of the antigen-antibody reaction? What is the reason for the extreme activity of the bacterial toxins? What is the role of peptides and proteins in the control of gene function? These are questions that may be answered in part when it becomes possible to synthesize readily the complex peptides and proteins involved in such reactions, and particularly when it becomes possible to prepare suitable analogues of these compounds.

Since the first synthesis of a peptide, glycylglycine, by E. Fischer and E. Forneau in 1901 [1], there has been a constant effort to develop new and better methods. There were many advances during the early 1950s, and the period culminated in the synthesis of the nonapeptide oxytocin by V. Du Vigneaud [2] and his colleagues. Since that time, continued progress on the synthesis of other peptides, particularly the peptide hormones, has resulted in the synthesis [3] of the adrenocorticotrophic hormone containing 39 amino-acid residues, and even of insulin containing two peptide chains of 21 and 30 amino acids [4, 5]. These were remarkable achievements indeed. They represented astute planning and required enormous expenditures of time, energy, and materials. For example, more than 200 separate steps were required for the synthesis of insulin. Thus the synthesis of polypeptides of this general size and complexity is possible, but the task is difficult. It was in an effort to overcome some of the many difficulties associated with the conventional synthetic procedures that a new approach, 'solid-phase peptide synthesis', was conceived and explored [6, 7].

The basic idea

The proposed method was based on the idea that it should be possible to assemble a peptide chain in a stepwise manner while it was attached at one end to an insoluble, easily filterable, solid particle, and that after the peptide with the desired amino acid sequence had been assembled, it could be removed from the supporting material and be isolated. In this way the soluble reagents and by-products could be removed at each step from the totally insoluble peptide by thorough washing. The advantages of such a scheme would be threefold: it should be possible to get high yields by forcing the reactions to completion; the number of steps, the difficulties of manipulations, and the overall time taken by peptide synthesis should be markedly decreased; and the losses of peptide at each step of the synthesis associated with conventional purification procedures should be eliminated. This concept was tested experimentally, and these several advantages were in fact realized.

The basic idea for solid-phase peptide synthesis is outlined in figure 1. The synthesis begins with a solid supporting particle and the introduction of a functional group, x, on to the solid. At this reactive site, the first protected amino acid is attached through a stable covalent bond. The protecting group is then removed selectively, exposing the reactive amino function. The first peptide bond is then formed between this amine and the activated carboxyl of the second protected amino acid. By alternately deprotecting and coupling with the appropriate amino-acid derivatives, the predetermined peptide sequence is built up in a stepwise manner. It must be emphasized that up to this point, the peptide chain has been in the solid phase at all times. It has never been in solution, and every reaction has involved one solid reactant. Furthermore, the intermediate peptides have not been purified in any way except by washing. Finally, the covalent bond holding the growing peptide chain to the solid is specifically cleaved. At this point, the peptide becomes soluble for the first time and enters the liquid phase. Suitable isolation and purification

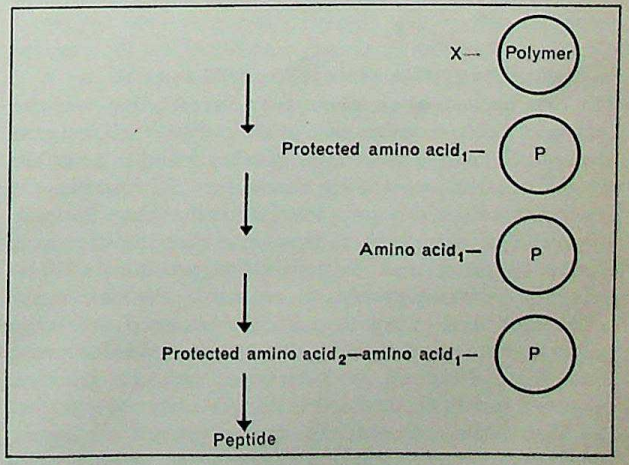


Figure 1 The general scheme for solid-phase peptide synthesis.

R. B. Merrifield, *B.A., Ph.D.*
Was born in Fort Worth, Texas, in 1921 and was educated at the University of California at Los Angeles. In 1949 he joined the staff of the Rockefeller Institute, where he is now Associate Professor of Biochemistry. His recent interests have been in the field of peptide isolation and synthesis.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

procedures are then applied in order to obtain the pure synthetic peptide.

In principle, the steps shown in figure 1 are simple and straightforward, but a considerable amount of exploratory and developmental effort was necessary to evolve a suitable working method. The various steps will now be examined and described in more detail.

The solid support

The selection of a suitable supporting solid was of first importance. It had to be completely insoluble in all of the solvents to be used, which included neutral, basic, and acidic organic solvents, and mineral acids. It had to have a stable physical form which permitted rapid filtration and at the same time provided a large effective surface. It also had to be easily substituted with a reactive group to which the peptide chain could be anchored. The solid that was most useful was a copolymer of styrene and divinylbenzene. It was obtained commercially in the form of small spheres about 10–80 μ in diameter. The properties of the polymer were determined in large part by the degree of cross linking, which in turn was determined by the proportion of divinylbenzene in the polymerization mixture. A 2 per cent cross-linked product gave a stable bead with a large effective surface. The polymer had a gel structure and swelled strongly in nonpolar solvents. This resulted in an increased permeability which made it possible to carry out a variety of organic reactions with the polymeric resin. Under proper conditions, virtually every aromatic ring could be substituted. This showed that the reactions were not restricted to the surface but occurred throughout the polystyrene network, and had the practical advantage that a convenient number of moles of peptide could be accommodated per unit weight of polymer. A useful range has been 0·05–0·5 millimole per g. If substitution had been limited to the surface layer, yields of only about 0·003 millimole per g would have been obtained.

Other polymers of styrene and divinylbenzene have been obtained with properties that made them promising possibilities for supports in solid-phase peptide synthesis. Among these were the macroreticular and macroporous forms, which have greatly increased surfaces because of large fixed internal pores. A third form, called 'popcorn polymer', containing only 0·5 per cent crosslinking, has been shown to be a useful support for the synthesis of a dipeptide [8].

Anchoring the peptide chain to the solid support

The first important reaction to be investigated was the linking of the first amino acid to the polymer. Here again certain criteria had to be met. The bond had to be stable throughout the succeeding reactions, and therefore it was important to rely on a covalent rather than an ionic linkage. It is important to recognize that the process is clearly different and distinct from processes of ion-exchange chromatography. In principle, the amino acid could be linked either through the carboxyl or amino group and the peptide chain could be assembled stepwise from the C-terminal or N-terminal end. In practice, however, it was preferable to link the carboxyl group of the C-terminal amino acid to the polymer. By doing so, the danger of racemization in subsequent peptide-forming reactions was minimized. The most likely bonds were, therefore, bonds through esters, amides, and perhaps hydrazides. In general, these would possess the necessary stability, but they had to meet the further requirement of being capable of selective cleavage at the end of the synthesis. This reaction, in which the completed peptide was liberated from the resin, had to proceed without cleavage at the peptide bonds or at other sensitive sites within the peptide.

Of the several modes of linkage investigaged, those using benzyl ester derivatives have been the most useful. They were particularly well suited for the purpose because they were stable to the deprotection and coupling reactions employed in the synthesis and because the completed peptide could be removed from the supporting solid by cleavage of the ester with hydrogen bromide or mild alkali. Only limited success has so far been achieved with phenyl esters followed by saponification, with benzyl amides followed by reductive cleavage, or with carboxylic-sulphonic dihydrazides followed by oxidative cleavage. These, and other schemes, merit further investigation, however.

To prepare the benzyl esters, the aromatic rings of the polymer were converted to substituted benzyl chloride derivatives by chloromethylation with chloromethyl methyl ether in the presence of stannic chloride catalyst. It was preferable to limit the reaction to about 5 per cent of the rings in order to prevent excessive substitution by peptide chains. The triethylammonium salt of an N-acylamino acid was then reacted with the chloromethylated polymer to give the desired benzyl ester.

Protecting the amino group

The choice of the amino-protecting group for the amino acids was of prime importance. The requirements were for a derivative that was stable and easy to prepare, that minimized racemization during the peptide-forming step, and that could be removed under conditions which avoided cleavage of the bond holding the peptide chain to the polymer. The carbobenzyloxy group, employed in Bergmann's well-known method [9], met the first three requirements very well and was acceptable by the last criterion under special conditions. Cleavage of carbobenzyloxy groups can, in general, be achieved by catalytic hydrogenation or by the use of anhydrous hydrogen bromide. However, hydrogenation was not feasible, because the required catalyst is a solid and is not effective when the substrate is also a solid. On the other hand, hydrogen bromide in glacial acetic acid was effective. Unfortunately, conditions which gave a quantitative scission of the carbobenzyloxy bond also caused an appreciable splitting of the benzyl ester holding the amino acid to the polymer. It was possible to overcome this difficulty by nitrating the polymer, since the resulting nitrobenzyl ester was much more resistant to attack by hydrogen bromide. This modification then required alkaline hydrolysis for the liberation of the completed peptide from the polymer. Such a scheme was used for the synthesis of the tetrapeptide, L-leucyl-L-alanyl-glycyl-L-valine, to be described later.

In an effort to improve the method, other protecting groups were examined. The formyl, trityl, and 2-hydroxy-1-naphthal derivatives were not successful under the particular conditions employed. There was, however, a very important improvement in the overall process when the *t*-butyloxycarbonyl group was used [10]. This was primarily because of the increased ease of cleavage

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

of the protecting group under mild acid conditions. In addition to greater acid lability, these derivatives also appeared to have all of the advantages of the carbobenzyloxy-protected amino acids. When the *t*-butyloxycarbonyl-protected amino acids were used, it was not necessary to resort to nitration of the polystyrene resin, as the unsubstituted ester was stable to the 1*N* hydrochloric acid required to remove the protective group from the product. It was then possible to liberate the completed peptide from the resin by means of hydrogen bromide in trifluoroacetic acid. Acid conditions were preferable to alkaline, because they eliminated the danger of racemization.

Formation of the peptide bond

The remaining reaction to be considered was the peptide-forming reaction itself. The requirements imposed by the solid-phase method were qualitatively similar to those for conventional methods but were more exacting. For example, it was absolutely essential that this reaction go quantitatively to completion. Unless this condition was fulfilled, mixtures of intermediates that were difficult to separate would accumulate. This was because the purification usually carried out at the intermediate stages of the synthesis is omitted in this process.

In the beginning, the most attractive derivatives were the active esters, especially the *p*-nitrophenyl esters [11]. While the first small peptides were in fact made this way, the results were not completely satisfactory. Under the particular conditions used, the reactions did not go to completion, and some racemization was observed. It has more recently been found, however, that both the nitrophenyl esters and hydroxyphthalimide esters [12] will react readily if the proper solvent is used. In dimethylformamide, both of these active esters gave quantitative yields of peptides. These reagents will probably become increasingly useful as the method finds wider application.

The first reagent which proved satisfactory [13] was dicyclohexylcarbodiimide. The excellent results with this coupling reagent easily offset the various objections which could be raised to it. The active intermediate formed between the diimide and the *t*-butyloxycarbonyl amino acid was extremely reactive and coupled very quickly with the free amine at the end of the peptide chain. Rate studies indicated that the reaction was complete even in this heterogeneous system within 30 minutes. The principal defect was the well-known intramolecular rearrangement which gives the acyl urea. This by-product could be separated readily from the peptide, but the side reaction was objectionable because it required the use of an excess of amino-acid reagent. The degree to which the reaction competed with the desired peptide-forming reaction varied with the different amino acids and was strongly dependent on solvent. Dimethylformamide favoured the rearrangement to the extent that a twofold to eightfold excess of reagent was needed to ensure complete acylation of the N-terminal amino acid. Methylene chloride minimized the reaction, so that a twofold excess, or less, was sufficient.

A test of the feasibility of the method

Let us now consider an experiment which was designed to test the idea in practice [7]. A very simple tetrapeptide, L-leucyl-L-alanyl-glycyl-L-valine, was chosen for this purpose. The peptide was prepared by a system that used nitrated polymer for the solid support, carbobenzyloxy as the protecting group, dicyclohexylcarbodiimide as the condensing reagent, and saponification for the peptide-liberating reaction. The completed peptide was purified by ion-exchange chromatography. For comparison, the same tetrapeptide was synthesized in the conventional way in solution by the nitrophenyl ester procedure [11]. The two products were indistinguishable when compared by quantitative amino-acid analysis, elemental analysis, paper chromatography, paper electrophoresis, counter-current distribution, and optical rotation. These results demonstrated the feasibility of the method. It was clear, however, that while the results were comparable to standard methods, both qualitative and quantitative improvements were required. The introduction of the *t*-butyloxycarbonyl protecting group, with its accompanying modifications, provided the needed improvements.

The synthesis of bradykinin and derivatives

It was recognized from the outset that to demonstrate the real value of the new approach it would be desirable to apply it to the synthesis of complicated peptides possessing biological activity. For this purpose the synthesis of the nonapeptide, bradykinin, was undertaken [14, 15]. Bradykinin was of interest for several reasons [16]. It is a peptide of moderate size and contains the polyfunctional amino acids arginine and serine, plus the imino acid proline. It is a biologically active peptide of considerable physiological importance, and the activity was expected to provide a specific test for the identity and purity of the product. Finally, it offered an opportunity to compare the solid-phase method with well-established procedures, since bradykinin had already been synthesized by conventional methods [17, 18].

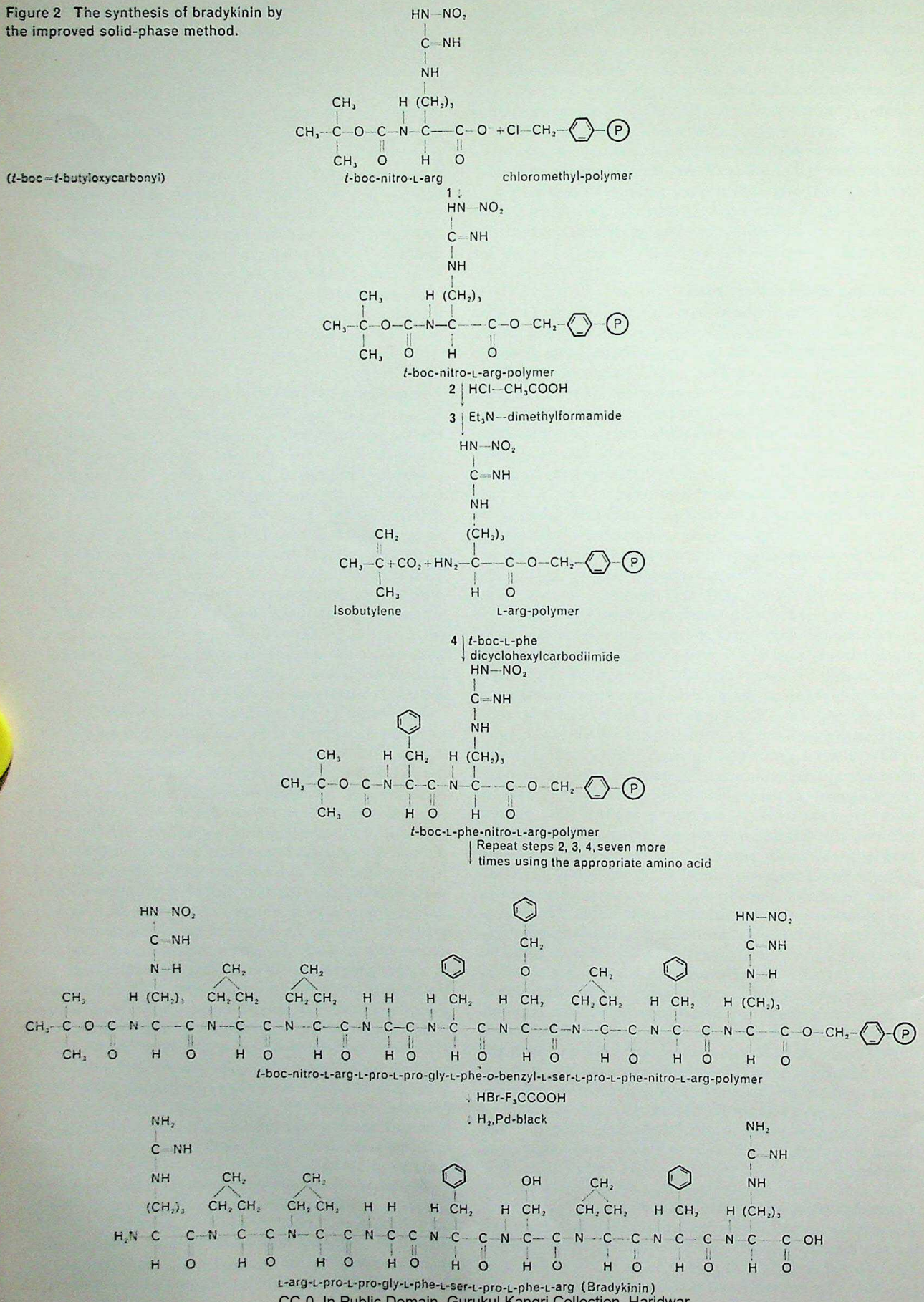
An outline of the synthesis of bradykinin by the improved procedure is shown in figure 2. A copolymer of styrene with two per cent of divinylbenzene was chloromethylated and then esterified with the triethylammonium salt of *t*-butyloxycarbonyl-nitro-L-arginine. The protecting group was removed with *N* hydrochloric acid in acetic acid, and the resulting hydrochloride was neutralized by treatment with an excess of triethylamine. The free base was then coupled with *t*-butyloxycarbonyl-L-phenylalanine with the aid of dicyclohexylcarbodiimide. These last three steps constituted one cycle of the synthesis, that is, the lengthening of the chain by one amino acid residue. The remaining residues were added in a similar manner by repeating the cycle seven more times, each with the proper amino acid derivative, to give the desired protected nonapeptide *t*-butyloxycarbonyl-nitro-L-arginyl-L-prolyl-L-prolylglycyl-L-phenylalanyl-*o*-benzyl-L-seryl-L-prolyl-L-phenylalanyl-nitro-L-arginyl-copolystyrene-divinylbenzene. The overall yield from *t*-butyloxycarbonyl-nitro-L-arginyl-polymer to the protected nonapeptide-polymer was essentially quantitative, according to amino-acid analyses. Since each cycle required only four hours, it was possible to complete two per day.

The peptide was cleaved from the solid support by passing a stream of hydrogen bromide through a suspension of the peptide polymer in trifluoroacetic acid. This reagent also cleaved the *t*-butyloxycarbonyl group and the ether bond in the *o*-benzyl serine residue. Catalytic hydrogenation with palladium black removed the nitro

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Figure 2 The synthesis of bradykinin by the improved solid-phase method.



CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

groups from the two arginine residues and gave free bradykinin. The yield and homogeneity of the product were remarkably good. After 26 separate reactions, with no purification procedures other than washing, a yield of 83 per cent was obtained, and over 90 per cent of this material was contained in a single component. This was demonstrated by electrophoresis and ion-exchange chromatography. Pure bradykinin (1·3 g per 10 g of supporting polymer) was isolated by use of a chromatographic column to give an overall yield of 68 per cent. The peptide was indistinguishable from authentic bradykinin as tested by paper chromatography, paper electrophoresis, and counter-current distribution. It was also pure as judged by amino-acid and elemental analyses. The final test of identity and purity rested on the biological activity of the synthetic peptide. The preparation was found to possess the full activity of bradykinin when it was compared quantitatively with an authentic standard in the isolated rat uterus assay and in the rat duodenum assay. Thus the synthetic peptide appeared to be pure bradykinin by both chemical and biological criteria.

A new plasma kinin was recently isolated from ox blood by D. F. Elliott, G. P. Lewis, and D. G. Smyth [19], and identified by them as methionyl-lysyl-bradykinin. This biologically active peptide was synthesized [20] using exactly the general method just described for bradykinin, but with certain added precautions. The ε-amino group of lysine was protected with a carbobenzyloxy group, and methyl ethyl sulphide was used in the cleavage step to prevent the formation of the benzyl sulphonium derivative of methionine. The undecapeptide was purified and isolated by procedures similar to those used for bradykinin. It was shown to be homogeneous and analytically pure and to possess the expected biological activity in the rat uterus test. This same peptide has recently been synthesized by classical procedures by E. Schröder [21]. These results demonstrated the applicability of the solid-phase method to the rapid synthesis, in good yield, of a pure peptide containing as many as eleven amino-acid residues, and showed that complicated amino acids such as methionine and lysine could be introduced into peptides in this way.

It was very important to know that racemization had not occurred during these syntheses, and the problem was examined in several ways. By quantitative measurements of biological activities, by optical rotations of products, and by degradations with specific enzymes, it was shown that no measurable amount of racemization had taken place.

Possible extensions of the method

One of the important questions remaining to be answered concerns the maximum size of peptide which can be synthesized by this procedure. Will the reactions fail to go to completion as the length of the peptide is increased, or will it become impossible to release the peptide from the supporting solid? The answers are not yet known. A preliminary experiment has shown that at least nineteen residues can be introduced into a peptide in this way, and it is expected that the useful range will be considerably greater. It may, however, become necessary to limit the growing peptide chains to the surface of the solid when the synthesis of very large peptides is attempted.

It seems pertinent to point out that this new approach to the synthesis of polypeptides should also be applicable to the synthesis of heteropolymers of defined structure in general, and to polynucleotides in particular. It seems quite reasonable to expect that some of the advantages which have been realized in peptide synthesis could also be found in a solid-phase polynucleotide synthesis. A simple, rapid, and efficient synthesis of these important compounds would be of enormous value in solving some of the fundamental problems of genetic coding and protein biosynthesis.

Automated synthesis

From the beginning, the main motivating force behind this work has been the possibility of developing a method for the automated synthesis of peptides. It was with this purpose in mind that the idea of utilizing a solid support was originally conceived. It appeared to offer the best possibility for simplifying the many operations to the extent that they could be controlled mechanically. With the device of anchoring the growing peptide chain to a completely insoluble particle, it became possible to conduct the entire synthesis of the peptide within a single reaction vessel. Once the first amino acid was attached to the solid and the product was introduced into the vessel, it was not removed at any time during the synthesis. All of the operations were thus reduced to the transfer of solutions to and from this reaction chamber. If automation can be achieved, it will become possible to attempt the synthesis of much larger peptides and hopefully to attack the problem of the total synthesis of proteins—the goal set long ago by Fischer [22].

References

[1] Fischer, E. and Forneau, E. *Ber. dtsch. chem. Ges.*, 34, 2868, 1901.
[2] Du Vigneaud, V., Ressler, C., Swan, J. M., Roberts, C. W., Katsoyannis, P. G., and Gordon, S. *J. Amer. chem. Soc.*, 75, 4879, 1953.
[3] Schwyzer, R. and Sieber, P. *Nature, Lond.*, 199, 172, 1963.
[4] Meienhofer, J., Schnabel, E., Bremer, H., Brinkhoff, O., Zabel, R., Sroka, W., Klostermeyer, H., Brandenburg, D., Okuda, T., and Zahn, H. *Z. Naturf.*, 18b, 1120, 1963.
[5] Katsoyannis, P. G., Fukuda, K., Tometsko, A., Suzuki, K., and Tilak, M. *J. Amer. chem. Soc.*, 86, 930, 1964.
[6] Merrifield, R. B. *Fed. Proc.*, 21, 412, 1962.
[7] *Idem. J. Amer. chem. Soc.*, 85, 2149, 1963.
[8] Letsinger, R. L. and Kornet, M. J. *Ibid.*, 85, 3045, 1963.
[9] Bergmann, M. and Zervas, L. *Ber. dtsch. chem. Ges.*, 65, 1192, 1932.
[10] Carpino, L. A. *J. Amer. chem. Soc.*, 79, 98, 1957.
[11] Bodanszky, M. *Nature, Lond.*, 175, 685, 1955.
[12] Nefkins, G. H. L. and Tesser, G. I. *J. Amer. chem. Soc.*, 83, 1263, 1961.
[13] Sheehan, J. C. and Hess, G. P. *Ibid.*, 77, 1067, 1955.
[14] Merrifield, R. B. *Ibid.*, 86, 304, 1964.
[15] *Idem. Biochemistry, N.Y.*, 3, 1385, 1964.
[16] Whipple, H. E. *Ann. N.Y. Acad. Sci.*, 104, 1, 1963.
[17] Boissonnas, R. A., Guttmann, St., and Jaquenoud, P.-A. *Helv. chim. Acta*, 43, 1349, 1960.
[18] Nicolaides, E. D. and DeWald, H. A. *J. org. Chem.*, 26, 3872, 1961.
[19] Elliott, D. F., Lewis, G. P., and Smyth, D. G. *Biochem. J.*, 87, 21P, 1963.
[20] Merrifield, R. B. *J. org. Chem.* 29, 3100, 1964.
[21] Schröder, E. *Experientia*, 20, 39, 1964.
[22] Fischer, E. *Ber. dtsch. chem. Ges.*, 40, 1754, 1907.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Meristems and the effect of radiation on cells

Digitized by Arya Samaj Foundation Chennai and eGangotri

F. A. L. Clowes

Ionizing radiation is extensively used in the treatment of cancer, and this is one reason for studying the effect of such radiation on living cells. The apical meristems of plants—the growing points of their shoots and roots—are particularly suitable for these studies. This is because cell division occurs principally at these points and the control of cell organization is simpler than in the bodies of animals. This article gives a description of the results of such studies, which include the discovery of the root tip's quiescent centre, and new ideas on cell organization.

The effect of radiation on apical meristems is now being extensively studied by those interested in cancer, as well as by botanists [1]. There is a number of reasons for this interest. Apical meristems are the permanently embryonic regions at the tips of the roots and shoots of plants. It is at these tips that cells divide, and it is here that all the growth in length, and much of the growth in thickness, of the plant occur. It is the behaviour of the cells of the meristems that determines what organs the plant will produce and how they will be constructed. The permanence of apical meristems and the relative simplicity of plant bodies make the meristems ideal systems for studying the control of organization, which is perhaps the next important problem for biologists to solve. Because ionizing radiations provide a way of interfering with organization, they help to find out about its control.

Most of the experimental work on meristems has been done on root tips, because these are simpler and more amenable to study than shoot tips. The root apical meristem consists of cells that grow and divide, and the resulting daughter cells may also grow and divide. Alternatively, they may grow and differentiate into the various kinds of cells possessed by roots. Some roots go on growing throughout the life of the plant, and in these the progeny of the dividing (or meristematic) cells always includes some cells that will also divide. There are 250 000 dividing cells in a root tip of the broad bean *Vicia faba*; about 125 000 in the root tip of maize *Zea mays*; and only a few thousand in the smaller roots of a fern such as *Marsilea* (figures 1, 2 and 4). In spite of its biological simplicity, the root tip is too complex to constitute a mathematically manageable problem in cell population kinetics without simplification.

Analysing the pattern of cells

The dividing cells are arranged in a pattern that differs in different kinds of plants (figures 1, 2 and 4). This pattern arises because both the planes of cell division and the rates of cell division are controlled in relation to the position of the cells within the root tip. In a median longitudinal section of a *Zea* root (figure 2), we see that the cells are arranged in files (figure 5). We can also see that there are three discrete regions of the root—the stele, the cortex, and the cap, which are quite distinct from one another—they each have their own initial cells and there is no exchange of cells between them. The central part of the cap consists of longitudinal files of cells, which indicates that the meristematic cells of this region divide mostly in the transverse plane, not longitudinally. This means that the initial cells of the central cap, those lying next to the pole of the cortex, do not grow transversely, for if they did, they would divide longitudinally, as the peripheral initials of the cap do, to compensate for the transverse growth. Plant cells are separated from each other by rigid walls through which strands of protoplasm pass. Thus they have to grow conformably with their neighbours and do not normally slip on one another. Therefore the fact that the central cap cells, just below the boundary with the cortex, do not grow transversely implies that the contiguous cortical cells also do not grow transversely and so do not divide longitudinally. We also know that they do not divide transversely because the cortex remains only one cell deep on the root axis sandwiched between the discrete stele and the central cap. These cells, therefore, at the pole of the cortical complex of cells, do not divide at all.

The quiescent centre

If we extend this analysis to the geometry of the *Zea* root tip, we can postulate a quiescent centre to the meristem in which cells rarely, if ever, divide [2]. This quiescent centre is a hemisphere containing about 600 cells in *Zea*, and it is surrounded by actively dividing cells (figure 5).

The existence of a quiescent centre can be confirmed by feeding the root with a radioactive precursor of DNA [3]. In meristems, such precursors are incorporated into the nuclei of cells only if the cell is preparing for division. The radioactivity, detected by a photographic film, therefore indicates which cells are meristematic. An autoradiograph of a root of *Zea* fed with tritium-labelled thymidine (figure 6) shows a region in which none of the cells have radioactive nuclei that coincides exactly with the quiescent centre predicted on geometrical grounds.

It is not possible to carry out so complete a geometrical analysis of the patterns of cells in root meristems for all species of plants. The pattern can be ambiguous, but the use of autoradiographs enables us to choose between the interpretations [4]. Most roots have a quiescent centre, though its size and degree of quiescence vary.

The technique of feeding meristems with radioactive precursors of DNA can also be used to measure the rate of cell division in different parts of the root tip. The rate at which nuclei become labelled in a region will give an estimate of the average rate of division [5]. Another technique uses mitotic poisons, such as colchicine. Colchicine stops the process of nuclear division by

F. A. L. Clowes, *M.A., D.Phil.*

Was born in 1921 and educated at Montrose Academy, Lawrence Sheriff School, Rugby, and Magdalen College, Oxford. He was a radar engineer during the war, has been on the staff of Manchester University, and is now University Lecturer in botany at Oxford. His chief research interest is in the development and organization of plants.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

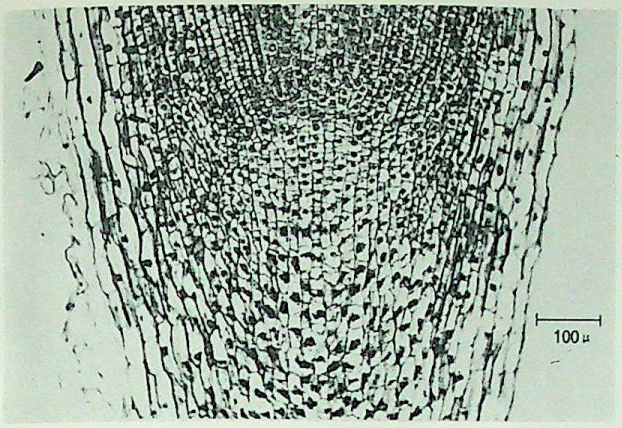


Figure 1 Root tip of *Vicia faba*, median section.

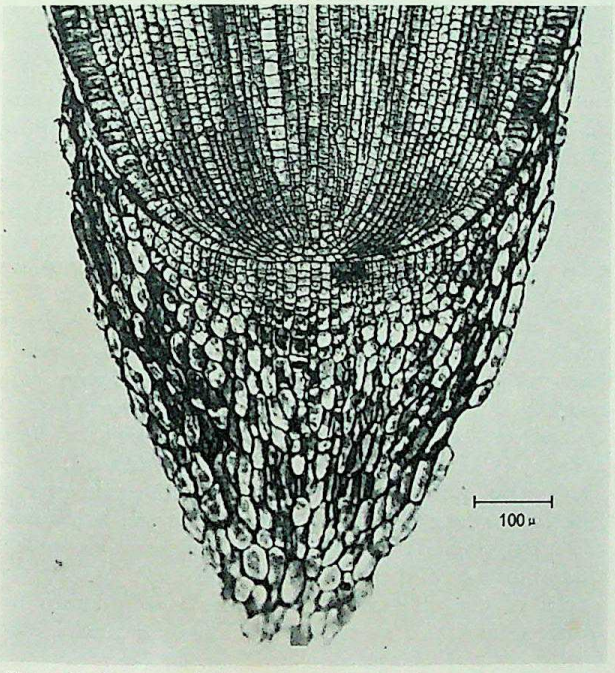


Figure 2 Root tip of *Zea mays*, median section.

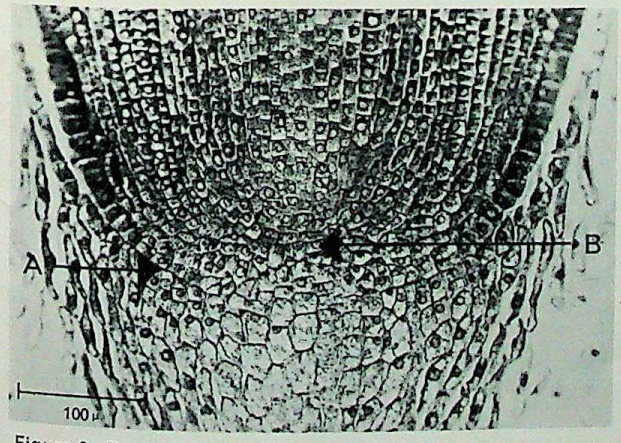


Figure 3 Root tip of *Zea mays* reorganized after heavy gamma irradiation. A, old cap boundary; B, new cap boundary. Compare with figure 2.

Figure 5 (right) Pattern of cell files in the root tip of *Zea mays* shown in figure 2.

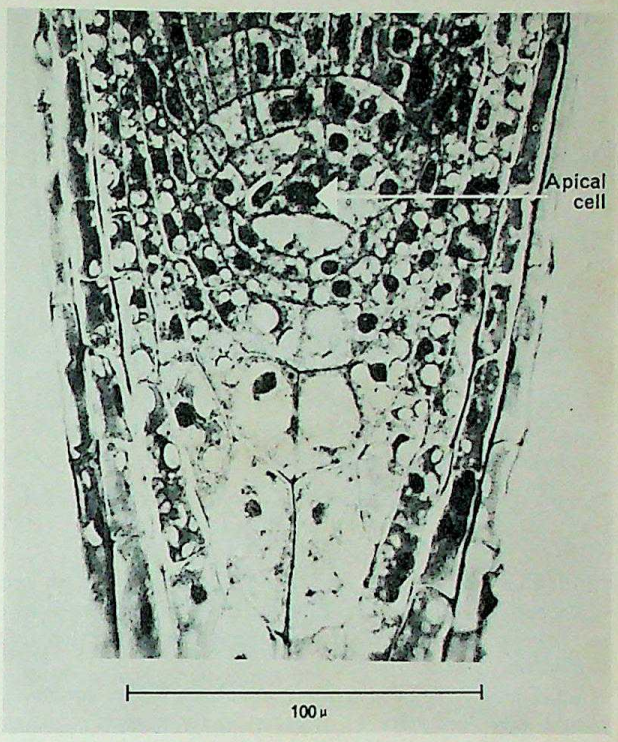


Figure 4 Root tip of *Marsilea* sp., median section.

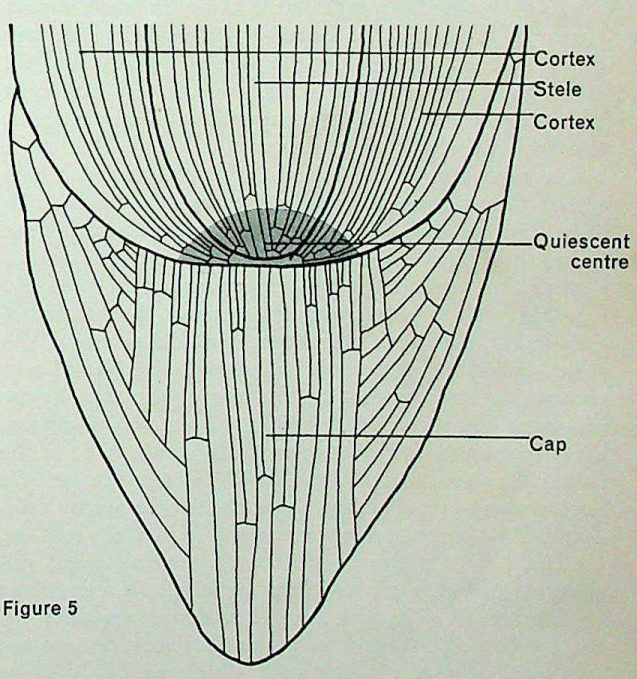


Figure 5

interfering with the separation of the chromosomes, but it does not affect the rate at which nuclei come into division. The rate of accumulation of the blocked stage of mitosis can therefore give us the rate of cell division. We might note here that counting the numbers of nuclei that are actually in division gives us no idea of the rate of division, because there is no time scale. Using these methods on *Zea*, we find that the fastest division goes on in the initial cells of the cap—those next to the cortex. For example, in one set of conditions they divide once every 12 hours, whereas the average rate in the adjacent quiescent centre is once in 200 hours. The cells of the stele just above the quiescent centre have an average

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

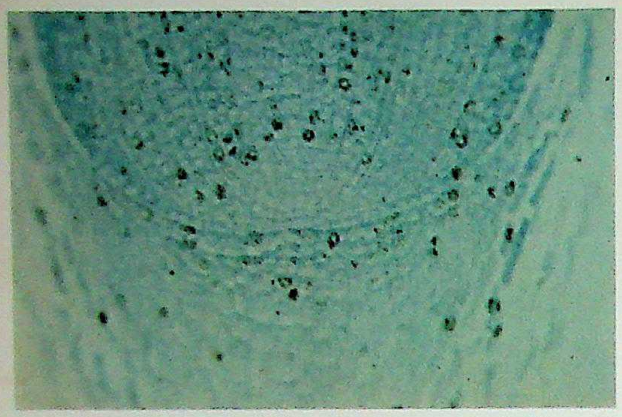


Figure 6 Autoradiograph of root tip of *Zea mays* fed with tritium-labelled thymidine for 24 hours.

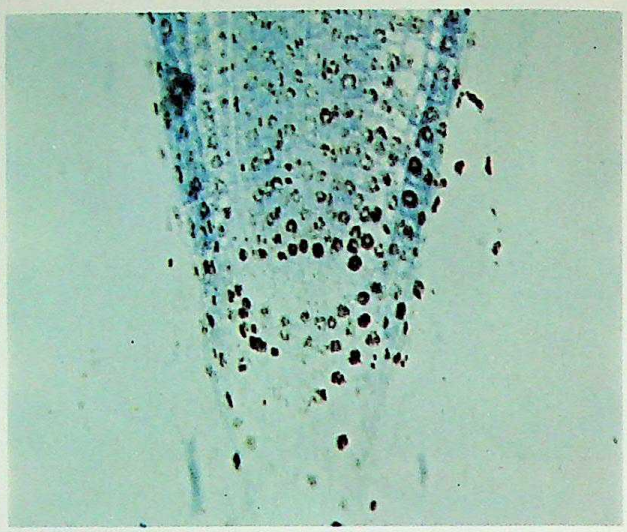


Figure 7 (right) Autoradiograph of root tip of *Sinapis alba* fed with tritium-labelled thymidine for 72 hours.

rate of one division in 28 hours. The relative rates are different in other species of plants. In *Vicia* there is not so sharp a distinction between the quiescent centre and the adjacent cells.

In the roots of some plants such as white mustard, *Sinapis alba*, cell division is more likely to occur during one part of the day than during the rest of the day. The quiescent centre is particularly clear in such plants (figure 7). This may be because the partial synchrony imposes special problems in the supply of substrates [6]. In *Sinapis*, the average rate of division in the quiescent centre is once in 500 hours, compared with once in about 30 hours in the adjoining tissues.

One objection to the concept of the quiescent centre is that the pattern of cells in the root tip leads us to believe that all the cells above the cap are derived from those at the poles of the stele and cortex (figures 1 and 2) —those that we believe on other grounds to be quiescent [7]. This objection is groundless because the pattern of cells in the meristem reflects the past behaviour of the plant, as well as its present behaviour. The files of cells converging on a region on the axis of the root in the quiescent centre are produced by the activity of cells at the initiation of the root, either in the embryo or in the primordia that initiate lateral roots. At these stages, the rudimentary apex is minute and all its cells are meristematic. If we consider the pattern of cells in a fern root tip, we can derive it from a single tetrahedral apical cell (figure 4). Such a cell divides so as to cut off a daughter cell from each of its four faces in a regular sequence. In roots of this kind there is no quiescent centre. Its position is occupied by the apical cell, which we know to be meristematic. But it would not alter the pattern of cells if the apical cell did not divide. The growth of the root would be carried on by the activity of the surrounding cells and the pattern would be identical, because it would have arisen from the apical cell, perhaps years previously, in the embryo or lateral primordium.

Irradiation of root tips

Work on the effects of ionizing radiations on root tips started because root meristems are convenient sources of dividing cells, and because chromosomes are clearly displayed only in the nuclei of dividing cells. In growing roots, about one-tenth of the cells of the meristem are in nuclear division at any one time. In other words, nuclear division occupies one-tenth of the cell cycle. Ionizing radiations damage cells largely by causing the chromosomes to break and behave in anomalous ways. The progeny of irradiated cells therefore often inherit unbalanced sets of genes. Some will be so unbalanced that the cells will die or will be unable to divide further. Others will show only minor mutations or none at all. The effect of radiation on root meristems has been extensively studied because, among other reasons, of the connections between ionizing radiation and cancer. However, until recently this work mostly concerned the chromosomes themselves, and problems of cell organization and population kinetics were inadequately considered.

If we feed a root of *Zea* with a radioactive precursor of DNA a few days after giving a heavy but non-lethal dose of X-rays, we find that the role of the quiescent centre and that of the rest of the meristem are reversed [3]. It is the nuclei of the quiescent centre that now prepare for division, and the normally meristematic nuclei stop synthesizing DNA and stop dividing. In *Zea* and plants with similar meristems we can see what happens. A group of cells in the quiescent centre multiplies and forms a virtually new root primordium that gives ries to all the normal regions of the root in continuity with the existing tissues. For example, a new plate of cap initials is produced and the growth of its progeny displaces the original boundary between the cap and the rest of the root (figure 3). Other parts of the old meristem are displaced also, though this is not so easy to see. In the root of *Vicia* there are no anatomically distinct boundaries between the regions of the meristem as there are in *Zea*, and it is very difficult to follow, by looking for the displacement of tissues, the growth of the new primordium formed after irradiation. This is unfortunate because most of the radiation experiments on roots use *Vicia* on account of its large chromosomes. However, it is possible to use the induced mutations in these large chromosomes to follow the course of development after irradiation.

The root produced after irradiation is often a chimera, that is, it consists of cells of two or more kinds which differ from each other by an inherited factor. This will occur if one of the irradiated cells has two of its chromosomes broken by the radiation and if the broken ends subsequently rejoin with the wrong pieces. Such a

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

mutation is not always lethal, and the cell may be able to divide normally. The progeny will exhibit the same aberration every time a nucleus divides. So, on the assumption that a particular aberration results from only a single accident, it is possible to trace the descendants of a single cell existing at the time of irradiation.

Investigations of this sort have been carried out by R. T. Brumfield, D. Davidson, and others in plants with large easily recognized chromosomes. In some roots, as much as a third of the new meristem has been found to consist of cells that are aberrant in one particular respect. This means that the root tissue produced after irradiation could be derived from as few as three cells that existed at the time of irradiation. It does not mean that normal, unirradiated roots have only three initial cells. In fact, the number of initial cells in a normal root is quite large—between 700 and 1200 in *Zea*—if we consider as initials all those cells lying next to the surface of the quiescent centre. The number fluctuates constantly as the root changes its width and as interchange with the quiescent centre occurs. Until the concept of the quiescent centre was put forward, it was difficult to reconcile the chimerical roots produced after irradiation with the large number of initials required by other evidence.

Differential radiosensitivity

The concept of the quiescent centre enables us also to understand how roots can survive massive genetic damage to their cells. Within a few days after a heavy dose of radiation, most root tip cells appear to contain damaged chromosomes. Yet, in spite of this damage, many roots continue growing after an initial check. H. A. McQuade and M. Friedkin showed, for example, that after feeding roots of the onion *Allium cepa* with tritium-labelled thymidine of high specific activity (0·89 Curies mM at 20 μCuries/ml), over 99 per cent of the cells contained visible defects in their chromosomes, due to the disintegration of the tritium atoms inside the cell nuclei. This seemed to imply such a heavy load of genetic damage as to make it impossible that the roots would survive. Yet roots do survive radiation from tritium-labelled thymidine of even greater specific activity [8]. Autoradiographs prepared after giving the roots a second labelling with a weaker solution show that the quiescent centre cells come into division and produce a virtually new root in continuity with the old root.

In this example, the quiescent centre would hardly be damaged by the very soft β-radiation from the first dose of tritium, for its cells do not incorporate the tritium into their nuclei because they do not synthesize DNA. The second dose of tritium, therefore, finds them undamaged, and they are stimulated to synthesize DNA by the disability of the normally meristematic cells.

This experiment is different from most irradiation experiments because, by using thymidine, a specific precursor of DNA, we select only some cells for irradiation. If we use an external source of penetrating radiation, such as X-rays, all the cells will be irradiated equally, the quiescent ones as well as the meristematic ones. Even so, the same regeneration from the quiescent centre occurs. Why are the cells of the quiescent centre less vulnerable?

Some workers believe that active, rapidly dividing cells are more susceptible to radiation damage than quiescent, slowly dividing cells [9, 10]. This view is known as the law of Bergonié and Tribondeau. It is generally true in man, where, for example, the bone marrow is much more sensitive than nerve cells. It has been suggested that this is the explanation of the success of radiotherapy for the treatment of cancer. Malignant cells divide without normal control at high rates, and on this theory they therefore are more vulnerable to radiation than normal cells. However, there has never been a wholly satisfactory explanation for the operation of the law, and some workers believe that it is unnecessary [11]. The permanent damage to a cell caused by radiation is displayed only after the cell comes into its first post-irradiation mitosis. This is because mitosis leads to the loss or rearrangement of pieces of those chromosomes that were broken by irradiation and it is this that strongly influences the reproductive future of the cell. Until mitosis occurs, the cell may have a full complement of genes controlling its activities and may behave normally. But, after mitosis, its daughter cells may be defective in their gene complements, and this will affect their ability to divide further. Thus rapidly dividing cells will display their radiation damage before slowly dividing cells. The damage to the slowly dividing cells may not show itself before the organ, or the whole animal or plant, dies.

The effect of irradiation on organization

Root tips provide one of the few multicellular, organized systems in which rates of mitosis are known for each part of the system. They are therefore highly suitable subjects for a study of the effect of irradiation on organization.

This study requires a measure of radiation damage to cells. The easiest to use is the fraction of cells with micronuclei. When a chromosome is broken by irradiation, it may rejoin. If it fails to do this, one piece of it will have nothing with which to attach itself to the mitotic spindle that pulls the chromosomes into two groups after they have divided. The fragment will often therefore be left out of the nuclei of the daughter cells. It will round itself off and lie in the cytoplasm surrounding one of the daughter nuclei; it is then called a micronucleus. Cells that have micronuclei as a result of irradiation must have been formed by a mitosis occurring after the irradiation, and their parent cell must have had a chromosome broken.

Figure 8 shows the percentage of cells with micronuclei in each of four parts of the root tips of *Zea* and *Vicia* after heavy irradiation. (*Vicia* is much more sensitive than *Zea*, and the two doses, 1800 rads to *Zea* and 360 rads to *Vicia*, are roughly equivalent in damage produced.) The percentages rise at first as cells come into their first post-irradiation mitosis, and then fall as the cells divide again without producing more micronuclei. The second peak is due to the cells whose coming into division is greatly delayed by the radiation, because they had not synthesized DNA at the time of irradiation [8]. It is clear that the quiescent centre is less susceptible than the rest of the meristem. This conclusion seemed likely from the reorganization observed in root tips. Moreover, the graphs give a clue to the reason for this. The second peak is higher than the first in the quiescent centre, especially in *Zea*, because these cells are mostly in the condition known as G_1—that is, their nuclei have only the amount of DNA endowed to them by their parent cells. They have not themselves synthesized any DNA. In other

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

parts of the meristem, some cells will be in G_1 and others will be in G_2 or mitosis after having synthesized DNA. These G_2 and mitotic cells have twice the DNA of the G_1 cells, and therefore present a bigger target to the X-rays. The measurements of the amounts of DNA per cell in root tips made by W. A. Jensen confirm this theory.

Maintenance at G_1, then, is probably the reason why the cells of the quiescent centre are less susceptible to irradiation than the rest of the meristem. Even a small advantage in favour of the quiescent centre could be critical, because plant cells are not mobile. It is therefore probably necessary for the new root primordium to be formed from a group of contiguous cells that are not badly damaged, and such a group is more likely to be found in the quiescent centre than elsewhere. The general cessation of cell division, which, as we have seen above, stimulates into division those cells whose reproductive potential has not been impaired, gives to the quiescent centre a timing advantage over any other group of contiguous cells that may subsequently be formed from an isolated, undamaged cell outside the quiescent centre.

Thus root tips obey the law of Bergonié and Tribondeau because they have a quiescent centre. We do not know if human tissues have anything comparable, but this seems possible in the light of the discovery of apparently distinct G_1 and G_2 populations of cells in mammalian epidermis by S. Gelfant [12]. The equivalent of a quiescent centre in human tissue, if it exists, may be of great importance in understanding radiotherapy and chemotherapy, although there is some reason to believe that the differential sensitivity of the phases of the cell cycle is not quite the same as in plant cells.

These radiation experiments have helped us to understand the normal control of organization as well as the effects of radiations. The existence of a group of cells held at G_1 may be advantageous to the root in various ways. The normal course in plant cells is for DNA synthesis to go on after cells have stopped dividing. The nuclei then become polyploid—they double or quadruple their number of chromosomes. This does not matter in cells that no longer need to divide, but could impose mechanical difficulties if they have to divide. In particular the germ tract, the cells from which the reproductive cells are formed, must remain diploid. But in roots with alternating periods of growth and dormancy the successful regrowth of the meristem probably also depends upon the reservoir of cells held at G_1 in the quiescent centre and thus unable to become polyploid.

In this article we have dealt only with acute radiation. Chronic radiation may impose quite different problems, for here quiescent cells may be more vulnerable than active ones. This is because the accumulated dose to a cell will vary with the duration of the cell cycle. Such studies will tell us more about organization.

The form of an organ depends upon the rates and planes of growth and division of the cells of the meristem forming it. In plants, there are none of the problems of cell mobility and adhesion that make morphogenesis in animals so difficult to understand. In both animals and plants, a particular cell must be able to ascertain its size in each dimension and its position before either setting in motion the processes that lead to division of the cell or

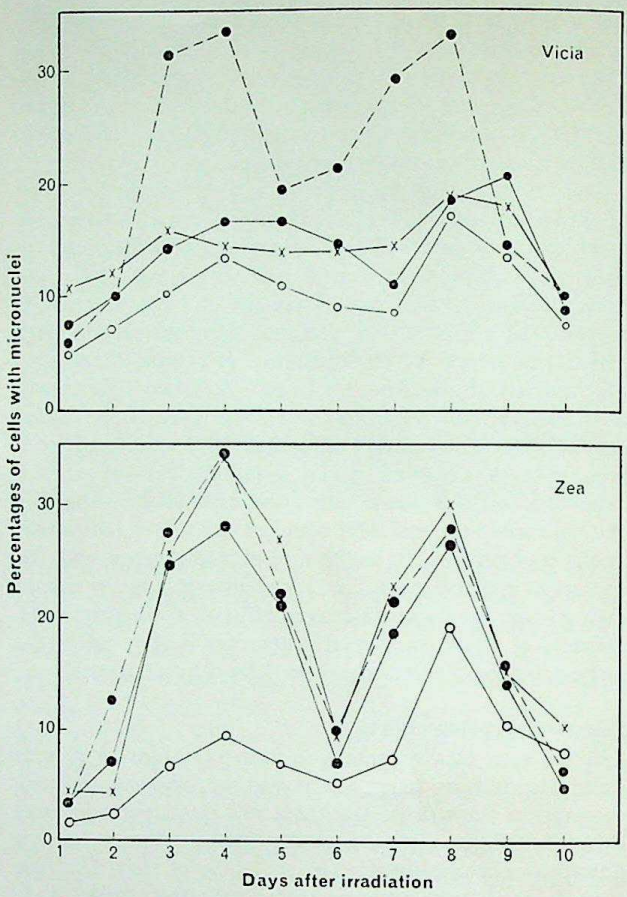


Figure 8 Amount of radiation damage at intervals after a single dose of X-rays (*Vicia*, 360 rads; *Zea*, 1800 rads) in four parts of root meristems. o——o, quiescent centre; ×——×, cap initials; •——•, stele just above quiescent centre; •– – –•, stele at 200–250 μ from quiescent centre.

repressing them. The information may be conveyed by feedback mechanisms whose nature we do not know. In the root tip we have a system whose programming is probably as complex as we can hope to study, but as simple as we can find among multicellular living things.

References

[1] Read, J. 'Radiation biology of *Vicia faba* in relation to the general problem'. Blackwell Scientific Publications, Oxford. 1959.
[2] Clowes, F. A. L. *New Phytol.*, 53, 108, 1954.
[3] *Idem.* 'Apical Meristems'. Blackwell Scientific Publications, Oxford. 1961.
[4] *Idem. J. exp. Bot.*, 7, 307, 1956.
[5] *Idem. Ibid.*, 12, 283, 1961.
[6] *Idem. New Phytol.*, 61, 111, 1962.
[7] Guttenberg, H. von. 'Grundzüge der Histogenese höherer Pflanzen'. Borntraeger, Berlin. 1960.
[8] Clowes, F. A. L. *Brookhaven Symposia in Biology*, 16, 46, 1963.
[9] Darlington, C. D. In 'Biological Hazards of Atomic Energy', p. 33. Clarendon Press, Oxford. 1952.
[10] Bond, V. P. In 'Radiobiology at the Intra-cellular Level', p. 55. Pergamon Press, London. 1959.
[11] Lajtha, L. G. *Progr. Biophys.*, 11, 79, 1961.
[12] Gelfant, S. *Expl. Cell Res.*, 32, 521, 1963.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Two memory stores in one brain

Digitized by Arya Samaj Foundation Chennai and eGangotri

J. Z. Young

The nature of the changes that occur in the brain when the memory stores a record are not known. In mammals it is not even clear where the record, which must contain discrete entities, is made. It is therefore interesting to find that the octopus brain has two almost separate stores, one for visual and the other for tactile information. Besides the lobes that carry the actual record, there are others concerned with reading-in or reading-out from the stores.

There is little agreement as to how to set about finding out what record is written in memory systems, nor even as to the best terms to use to discuss the problem. The nervous memory, like the hereditary memory (the nucleic acids of the chromosomes), provides the animal with instructions that enable it to survive and reproduce in a particular environment. The hereditary memory system is 'taught' only by the relatively slow and random processes of mutation, recombination, and natural selection, but the special feature of the nervous memory is that its information can be kept up to date. The nervous memory system includes specific equipment for receiving signals that quickly indicate the results of the actions that the animal has taken. Thus there are nerve fibres that signal pain, whose specific and only function is to indicate that what the organism is doing (or has just done) is likely to damage it. Conversely, there are nerve fibres of taste that send signals when acceptable material has been taken.

The information provided by these 'signals of results' is used by the brain partly to initiate reflexes, say withdrawal or eating; but the brain also establishes a memory record as a guide to future action. The study of the equipment that makes this possible is an essential preliminary to a search for whatever material change in the brain constitutes the memory record. In spite of the work of generations of psychologists and physiologists, it has not yet been established how the various parts of the brain collaborate in the 'writing' of this record. Indeed, it is not yet known whether the records of past events have particular locations in the brain. There are indications that the record for each event is widely spread. For example, removal of a particular part of the cerebral cortex of a man or other mammal does not usually lead to failure to recall certain events while leaving the memory for others intact. Yet of course there must be a highly specific set of records in the brain. A man can recall accurately the details of individual events that occurred at numerous particular single moments in the past. There must therefore be a record that contains a corresponding number of discrete entities of some sort.

The two memory stores in the brain of an octopus

This encourages one to believe, despite previous disappointments, that the location of the memory system can be discovered by a sufficiently determined search. Indeed, after some years of work on the brain of the octopus we can now see rather precisely the location of two quite distinct memory stores. One of these records the results of actions that have followed events seen with the eyes, the other of actions following the touching of particular objects with the arms (figure 1). These two stores provide a splendid opportunity to study the characteristics of the nerve cells that constitute the memorizing apparatus.

This is not to say that the problem becomes simple. Indeed, one of the interesting things about the octopus is that each of its two memory systems is provided with no fewer than four distinct auxiliary lobes. These are constructed on the same plan in each of the two systems, and we can experiment to show what roles they play in the whole process. The presence of so many distinct parts in each memory system goes some way to explain why the memory record seems not to be highly localized. Interference with any of these parts may impair the whole process of recording and the later use of the record.

In computer memory systems, we can distinguish between the actual record, say on magnetic tape, and the equipment for 'reading-in' to it or 'reading-out' from it. This equipment must be able to find the appropriate 'addresses' in the memory—for example the parts of the tape that contain the records of particular events. We are

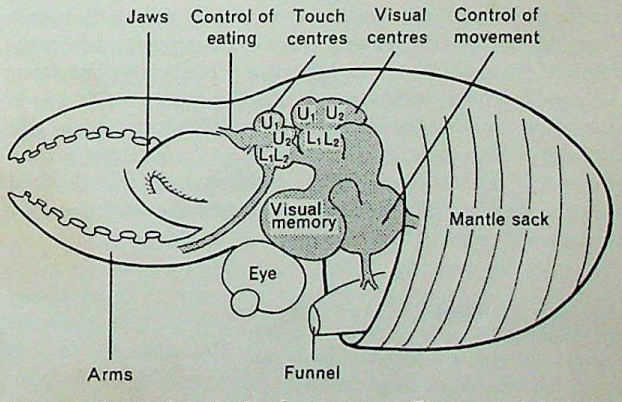


Figure 1 Parts of the brain of an octopus. The centre labelled 'visual memory' is the optic lobe, which also serves for classifying the visual input and for other functions.

The four lobes labelled 'visual centres' are arranged in lower and upper pairs (L_1 and L_2, U_1 and U_2). The lower centres (L_1 lateral superior frontal, and L_2 subvertical) serve as amplifiers of the tendency to attack objects in the visual field. The upper centres (U_1 median superior frontal, and U_2 vertical) play a part in the tactile as well as visual memory.

In the touch system, L_1 (lateral inferior frontal) and L_2 (posterior buccal) correspond to the lower visual centres, except that L_2 contains the touch memory store, there being nothing comparable to the optic lobe. The upper touch centres U_1 (median inferior frontal) and U_2 (subfrontal) are concerned with only the tactile memory system.

J. Z. Young, *M.A., F.R.S.*

Was born in 1907 and was educated at Marlborough College and the University of Oxford. He worked for two years at the Marine Biological Station at Naples, afterwards returning to Oxford, where he became Fellow of Magdalen College and University Demonstrator in Zoology. He is now Professor of Anatomy at University College, London. His research work has been on the microscopic structure and function of various tissues, especially in the nervous system. Since 1950 he has been conducting research into the nature of memory systems; the behavioural studies in this work are carried out at Naples.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

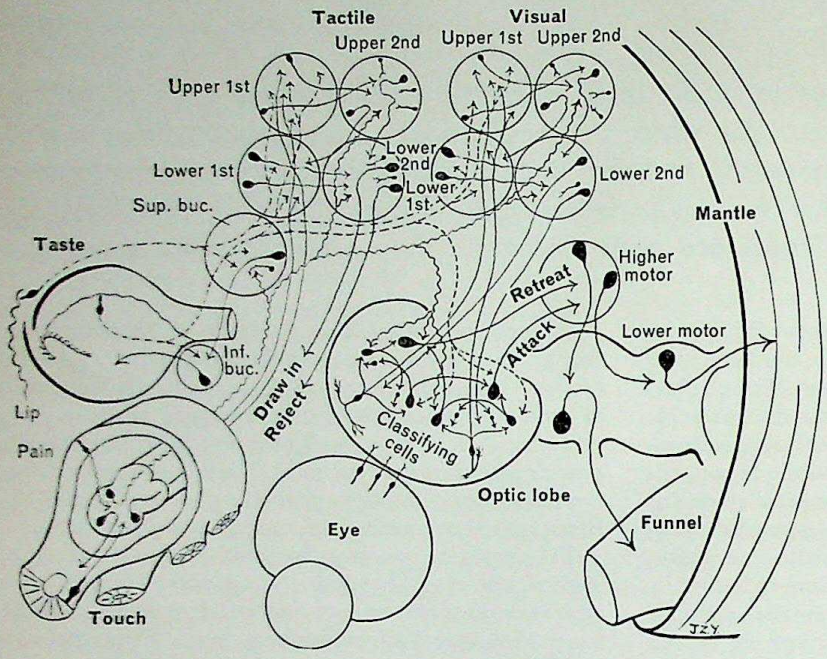


Figure 2 Diagram of the connections involved in the two memory systems of an octopus. All the pathways shown have been proved to exist except those leading to the small cells in the optic lobe. However, it has not been shown by physiological means that the dotted pathways actually carry taste signals or those with wavy lines pain signals. The two systems are shown somewhat more separated than they really are. The visual centres send some fibres to the tactile ones, and removal of them affects tactile learning.

so far from understanding neural memory systems that it still has to be shown whether they actually contain parts with the functions of finding addresses and sending signals to them or from them. However, it is hard to see how any recording system can dispense with such equipment, and we have some evidence that the functions of the four lobes associated with each of the two memories of an octopus include reading-in and reading-out.

There are, however, even more fundamental questions to be asked before we can hope to find where the memory record is made. What sort of a record is it? In particular, are signs or symbols selected from a code in order to record the occurrence of individual external events? In writing a book, information is stored by selecting words from the code that is provided by the previously established conventions as to the use of certain physical signs. Other artificial memory-systems function similarly. Is there any such set of items, pre-established in the brain, among which selection is made for recording in the memory? Further, how is it indicated that individual events were 'good' or 'bad' and hence should be sought or avoided when they recur?

If information is stored by selecting appropriate items from a code set, the essential first step in the search for the learning mechanism should surely be to 'break the code', that is, to find out what features are used by an animal or man in, say, the identification of a visual shape. Having done this, we may be able to find the code signs that stand for these elements in the brain.

The code of the visual system of an octopus

Experiments with octopuses have had some success in breaking the visual code. The animals recognize shapes partly by, in effect, measuring their vertical and horizontal extents [1]. It was found that in the optic lobes of the animals there are cells with dendrites so orientated that each cell will signal only when a pattern of light with a particular orientation falls upon the retinal cells connected to it (figure 8). We can therefore call them classifying cells. In the cat there is striking experimental confirmation that cells of the visual cortex are activated or inhibited only by a pattern of light with a particular orientation (figure 3).

The receptive field systems of neurons have been

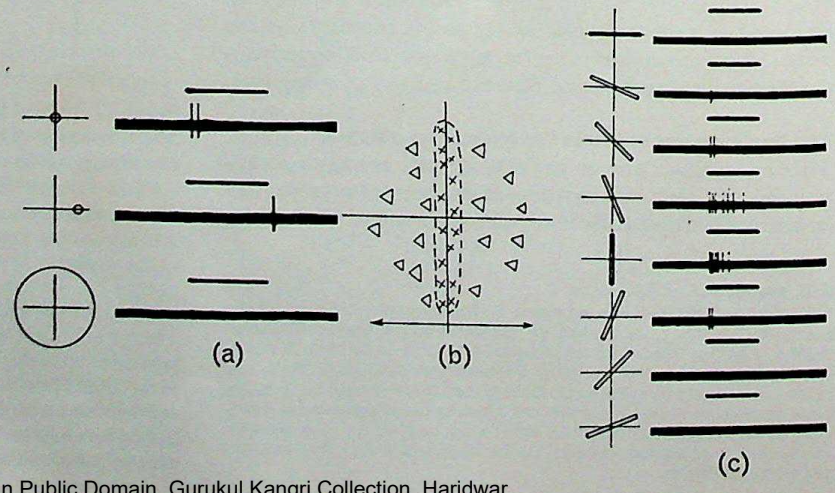


Figure 3 Experiment to show orientation of receptive fields of cells in the visual cortex of a cat. A microelectrode has been inserted into a single cell and the strokes on the lines of the oscillograph sweeps indicate when it passes signals. At the left (a) is the result of shining small spots of light on to various parts of its visual field. Light at the centre of an oval field excites it to fire, light to the side of the centre inhibits it (Hubel and Wiesel, *J. Physiol.*, 1959). The cell therefore serves as a detector of a vertical contour. The parts of the field that are stimulated are indicated by 'x' in the centre figure (b); those that are inhibited by ◁. As shown at the right (c), when an illuminated slit is used, the cell signals only when the slit is vertical.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

shown to be orientated in various nervous tissues. In the optic lobes of *Octopus* they have the appearance of a grid (figure 7). Orientated fields have also been found in various parts of the mammalian cerebral cortex (figure 16). There is therefore some reason to believe that this rather simple geometrical feature may provide a part of the set of code elements with which the memory record is built. Of course there must be cells that encode other features. Some presumably respond to particular levels of brightness, others perhaps to sharpness of angles, extent of outline, and other features of the figure. The outputs of the primary classifying cells may be combined in various ways by higher orders of classifying cells, each responsive to particular patterns of activity in the antecedent layers. In our ignorance of these cells it is difficult to be explicit about this, but it is perhaps possible to see how systems representing particular patterns at the receptor surfaces would be detected. The point is that each brain is provided with a set of detectors able to respond to particular features of the environment that are likely to be relevant to the life of the species. The set is presumably provided by heredity, and modified over the generations by natural selection. Moreover, the various combinations that occur during each individual life presumably themselves modify the classifying system by the process of learning described below. There is thus built up what might be called a 'model' in the brain—a representation of what has been learnt [2]. Hebb has expressed a somewhat similar concept by saying [3] that cell assemblies are built up in the brain. His concept is more dynamic than the present one which, although specific, may be imperfect as a representation of the constantly changing activities of the brain.

Learning by closing unused channels

In order that the members of the classifying set shall establish a record or representation of the results of past events, each of them must be able to produce two alternative outputs. Thus a cell of the optic lobe of the octopus that records 'horizontal' has possible outputs that lead either to the motor mechanism for attack or to that for retreat (figure 2). Suppose that, following the appearance of a horizontal rectangle in the visual field, an attack is made and food is obtained. The taste receptors in the lips and buccal mass signal the occurrence of food, and these signals have somehow to increase the probability that when the 'horizontal' cell is activated on a subsequent occasion, an attack will be produced. My suggestion is that this may be effected by reducing the probability that the opposite, retreat, pathway is activated. Collaterals of the attack neurons may do this, perhaps acting through the small cells that accompany the large ones at the centre of the optic lobe (figure 2). It may be that these small cells have the specific function, when appropriately activated, of rapidly changing their metabolism so as to produce a lasting inhibition that blocks the unwanted pathway.

If the system suggested here is approximately correct, it means that on each occasion of learning the probable output of a proportion of the classifying cells is altered. The gradualness of learning then consists in altering the pathways from sufficient of the classifying cells to provide a reliable response. Each single occasion of learning must leave its record and may in principle be recalled under suitable conditions.

This system of learning what not to do may seem paradoxical, but the exclusion of one possibility is of course a necessary corollary of any choice. In the classical conditioned reflex, the ringing of a bell can potentially make the dog salivate either more or less, for conditioning can proceed in either direction. If meat follows the ringing of a bell the system learns not to salivate less.

Paired circuits for distributing the signals of results

As outlined so far, the learning mechanism is, of course, absurdly simplified. Even in an octopus we have found that a complex system of auxiliary equipment is involved. There are lobes concerned with what we may call approximately 'addressing' and 'reading-in' to and 'reading-out' from the memory. These terms are not entirely applicable, nor indeed adequate, to describe the many functions of these masses of nerve cells.

Fortunately, it has been possible to work out the plan of the connections in considerable detail [4]. In both visual and tactile systems, the centres are arranged to form two tiers of circuits, each consisting of two units. The first lobe receives its input from the optic lobe and the second, lower, lobe sends its output back to the optic lobe (figures 2 and 9). In addition, the circuits receive tracts of fibres from the lips and mouth, to signal taste; and others that are presumed to signal pain. In the visual system, it is possible to break the lower circuit surgically, and after this operation the octopus shows no gross aberrations. It is not blind, and will put out an arm to take a crab that appears near to it, but it never launches out, as a normal octopus will do, to attack a crab that appears at a distance. This circuit therefore serves to provide the 'amplification'—multiplication—of visual signals that is necessary to initiate an attack.

The upper pair of lobes is still more interesting and plays an essential part in the memory. Inputs are received from the lower circuit and the output is returned there. The upper loop is thus, as it were, in parallel above the lower (figure 2). The mixed optic and tactile fibres of the lower circuit continue, with much further interweaving, into the first lobe of the upper one. The receptive fields of the cells of the latter thus allow combinations of visual inputs to be associated with taste. The output fibres of the first lobe of the upper circuit interweave to allow further recombinations as they pass on into the second lobe of the upper circuit (figures 11 and 13). This second lobe, called the vertical lobe, is composed of an immense number of minute cells and a few whose fibres go down into the lower circuit and thus back to the optic lobe (figure 14).

The hypothesis is that this upper circuit allows for the signals of taste and pain to produce their effects in the memory. The circuit serves to amplify the tendency to attack objects appearing in the visual field—except when pain is present. In that case, the circuit enables the animal to learn not to attack that figure. After an interruption of the upper circuit, an octopus shows no superficial abnormality of behaviour, but there are subtle yet definite alterations of what might be called 'motivation' or the strategy of attack. There is also serious impairment of the ability to learn. After removal of the vertical lobe, the animals can be described as uninhibited—they come out very readily to attack any object that moves in the visual field. Thus they persistently attack crabs even if they are given electric shocks when they do so. The

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

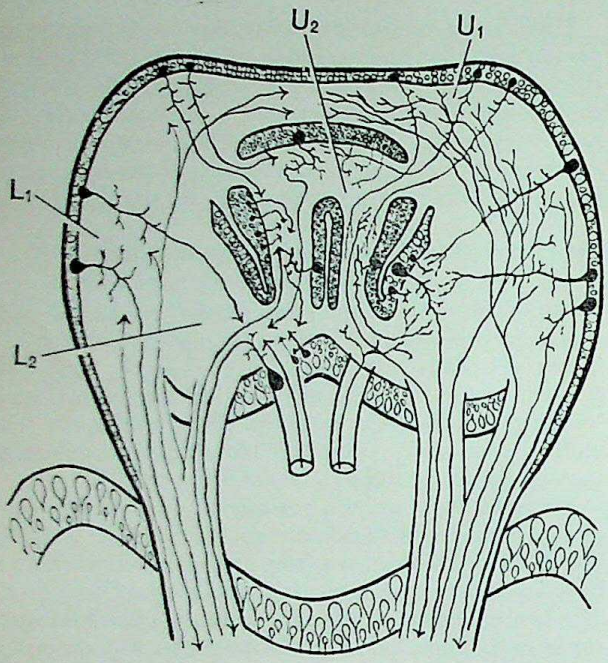


Figure 4 Diagrammatic drawing of tactile system from cells stained by Golgi's method.

vertical lobe therefore seems to be concerned with ensuring that the signals of pain become properly available to perform their function in the memory system.

Short-term memory systems

Some system for 'mixing' the signals from the receptors for taste and pain with those from the eye must be an essential feature of any visual memory. The upper visual circuit has this as its basic function, but it has others that are equally important. The signals that come from an object detected at a distance inevitably reach the brain some time before the signals of taste or pain that indicate the results of whatever action the animal has taken concerning the object. The delay may be long or quite short, but the animal must learn that features that were seen some time earlier were followed by good or bad results. This time-gap can be bridged only if there is some short-term memory system that holds what we may call the addresses of the classifying systems that were stimulated and then delivers to them the signals of pleasure or pain when they eventually arrive. There is some evidence that the self-re-exciting circuit arrangement of the vertical lobe system functions in this way. Animals in which it has been interrupted are unable to set up some types of new representations in the memory if the intervals between rewards are greater than a few seconds.

Similar short-term memory circuits certainly exist in mammals, including ourselves. The centres of the limbic system, below the cerebral cortex, have long been known to be organized to form circuits that re-excite themselves. Activation of them has effects, such as 'eating', 'rage', and 'escape movements' that would follow from what are here called signals of results. The 'centres' are often arranged in pairs. For example, after removal of the ventro-medial hypothalamic nucleus, a rat may eat large quantities although already filled with food. After injury to a point a few millimetres more laterally it will take neither food nor drink, and dies from starvation. Moreover, some of these hypothalamic-hippocampal circuits are also concerned with memory. If they have been damaged, the patient may be unable to set up any new records of past events, while retaining perfectly well what had previously been learned [5]. The gaps in the memory record that follow a blow on the head are a further example of the necessity for some circuit to maintain the representation for a period while it is being 'printed'.

There is therefore much to suggest that understanding of the complex phenomena that are rather loosely called 'motivation', 'drive', and 'emotion', and their connection with memory may be made much more precise by study of such circuits. The basic problem of the design of an exploratory, self-teaching homeostat is presumably similar in all animals, and we can learn about such systems by studying any examples that are available.

Failures of the memory system after injuries to the paired centres

In octopuses, the upper visual circuit plays a complex part in both reading-in and reading-out. One of its

Figure 5 Transverse section across the optic lobe. Stained with silver (Cajal's method) so that the nerve fibres are black, nerve cells orange. The section shows only the general plan of the lobe. The nerve fibres from the eye enter at the right (opt. n.) and end in the outer layers of the lobe (plexiform zone, pl.). Here they meet the receiving dendrites of cells lying deeper in the lobe, which send signals inwards. The centre of the lobe is occupied by islands of cells with fibres between them. (×17)

Figure 6 Higher-power view of outer part of optic lobe, stained as figure 5. The optic nerve fibres (opt. n.) pass in to the plexiform zone (pl.). The dendrites of the next cells in the chain (den.) come up from deeper in the lobe and spread out in the tangential layers of the plexiform zone (tan.). (×250)

Figure 7 Section tangential to the plexiform layer of the octopus optic lobe (Golgi's method). The fibres shown are the main dendrites of cells such as those of figure 8. They form roughly a rectangular grid. (×280)

Figure 8 The receptive dendritic fields of three of the 'classifying cells', spreading in the plexiform zone. The sections are cut parallel to the tangential layers. The stain has the property of picking out individual nerve cells (Golgi's method). The outlines of the fields are shown with dotted lines. (×150)

Figure 9 Longitudinal vertical section through the brain of an octopus, stained with Cajal's method. Showing the centres connected with the visual and tactile memory systems. Not all can be seen in one section, and the two lower first centres, (L_1) lateral inferior frontal and lateral superior frontal, do not show. The two lower second centres (L_2), posterior buccal and subvertical, have large cells and hence appear pale. The two first upper centres (U_1, median inferior frontal and median superior frontal) show interweaving bundles of fibres. The two second upper centres (U_2) contain masses of minute cells, showing as dark outer layers. (×15)

Figure 10 Horizontal section through the visual centres showing the fibres entering the lower first centre at the sides (L_1) and proceeding on to the interweaving bundles of the upper first centre (U_1). The fibres from the lower first to the lower second centre (L_2) can also be seen. (×25)

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

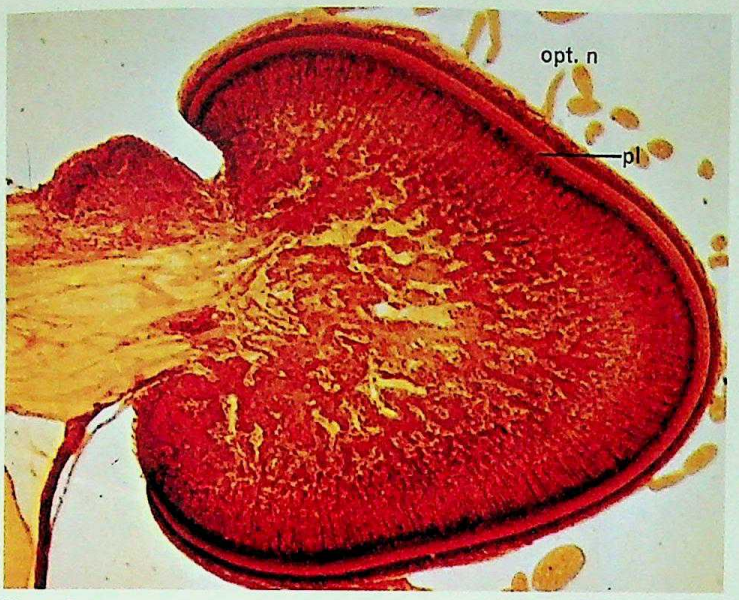
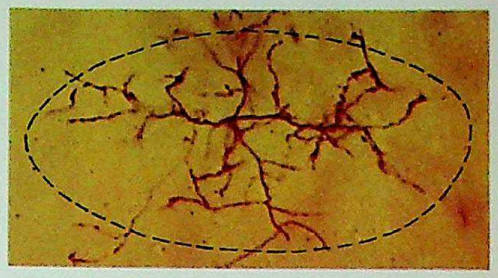
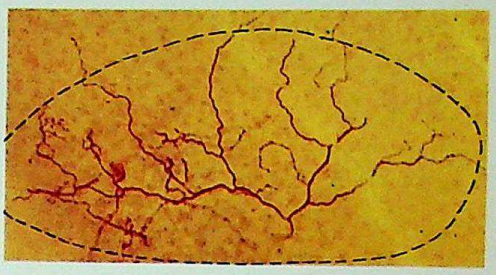


Figure 5





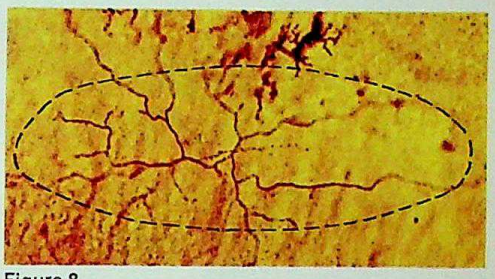


Figure 8

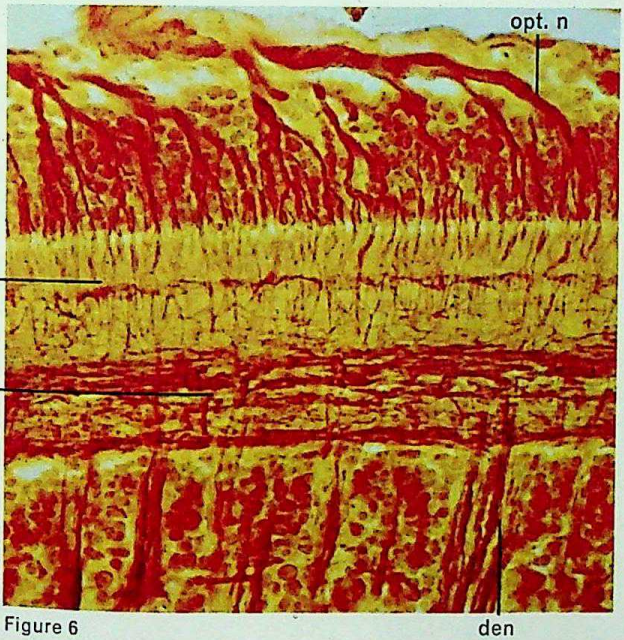


Figure 6

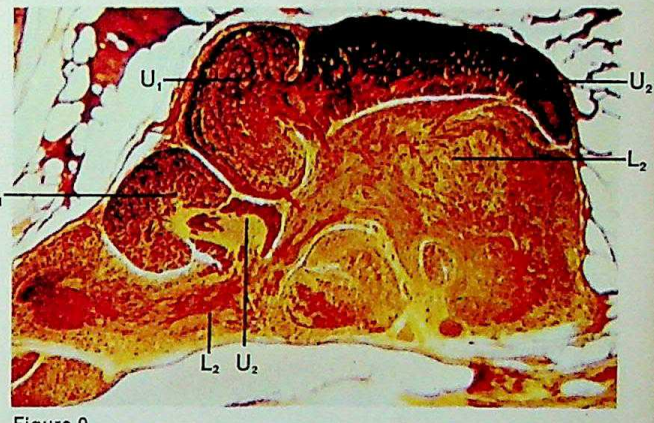


Figure 9

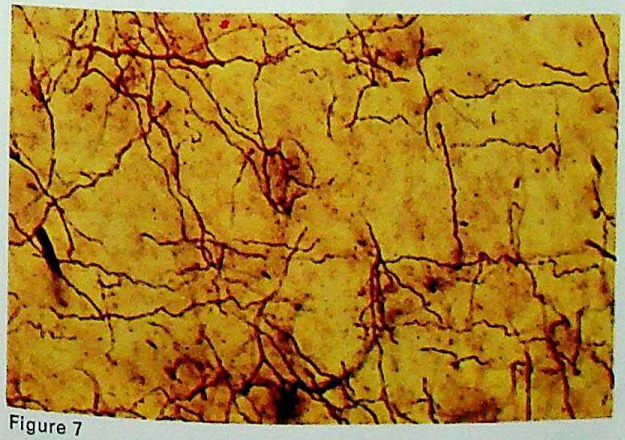


Figure 7

Figure 10

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

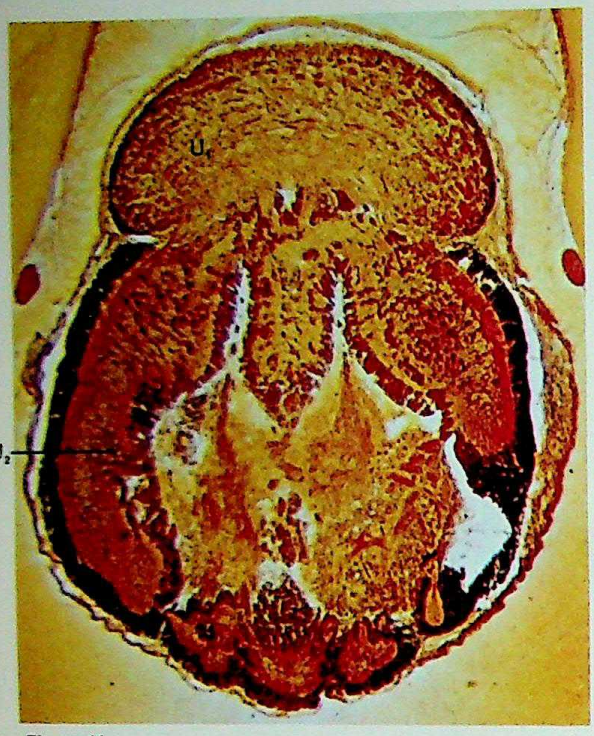


Figure 11

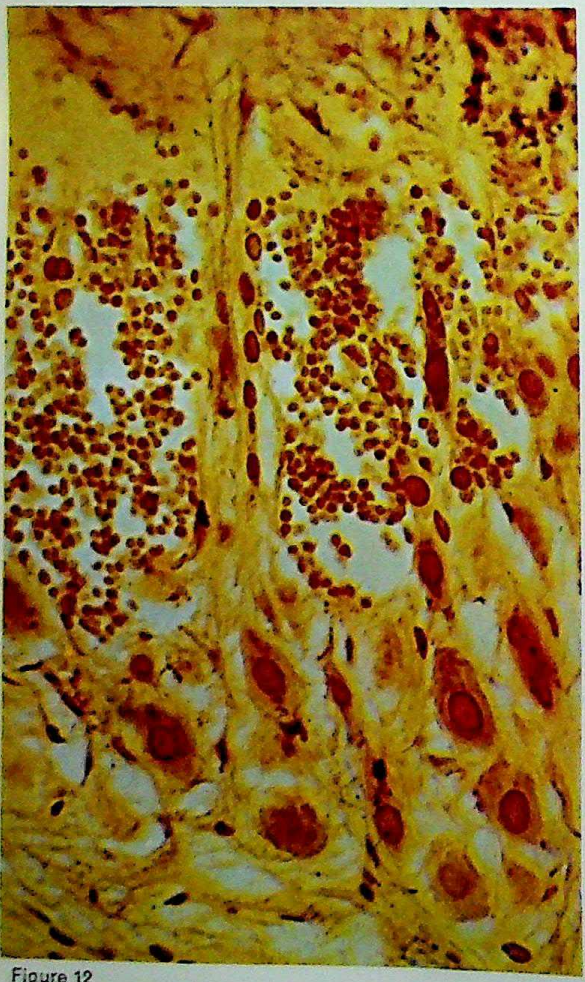


Figure 12

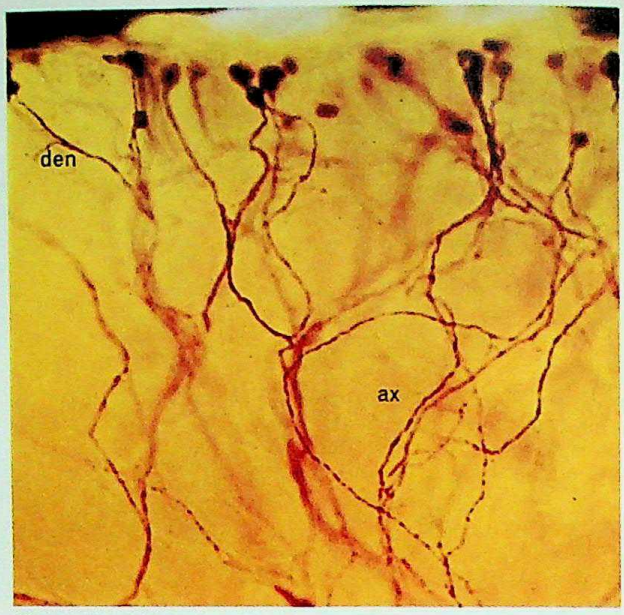


Figure 13

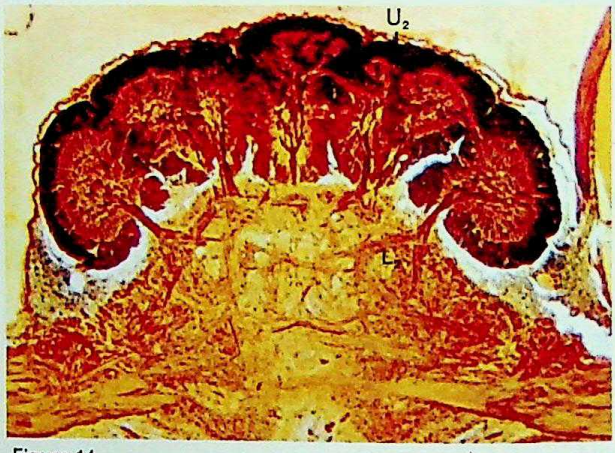


Figure 14

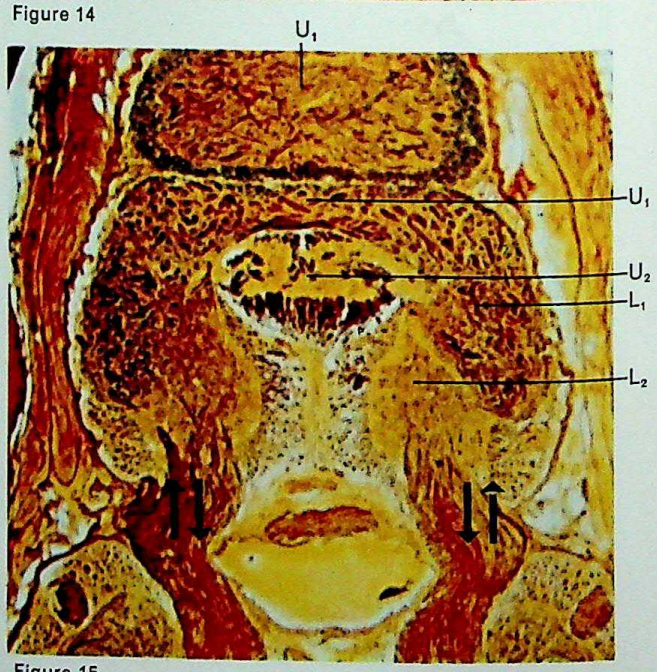


Figure 15

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Figure 11 Horizontal section to show the interweaving bundles of fibres passing from the first (U_1) to second (U_2) upper visual centres (Cajal's method). (×30)

Figure 12 Cells from the region of the tactile system that probably actually carries the memory record. Only the cell bodies are seen. The connections are in the tangle above (Cajal's method). (×500)

Figure 13 Individual cells of the upper first visual lobe, showing their receptive dendrites (den.). Their output fibres, axons (ax), interweave on their way to the second upper centre (Golgi's method). (×250)

Figure 14 Transverse section showing the bundles descending from second upper (U_2) to second lower (L_2) centre. From the latter, fibres pass back to the optic lobe (see figure 2). (×12)

Figure 15 Transverse section of the lobes of the tactile system. Nearby all the connections are shown except that between U_2 and L_2. The arrows show the pathways of fibres to and from the arms (Cajal's method). (×17)

functions is probably to increase the number of cells representing particular features of a situation that are 'conditioned' as a result of a single occasion of learning. After its removal, an octopus is no longer able to perform, using one eye, tasks learned only with the other [6]. In other words, this circuit assists in the 'generalization' and 'transfer' of the record that has been learnt. Many of the fibres running between its lobes cross the mid-line, as also do fibres leaving the system for the optic lobes.

Injury to the vertical lobe produces such profound effects upon learning that it is not surprising that Boycott and I were tempted for a long time to consider the lobe as the seat of the memory record. After its removal, octopuses were unable to learn to discriminate between, say, horizontal and vertical rectangles if these were shown successively and one of them yielded food and the other a shock. However, even animals that seemed to have learned nothing during such training would perform correctly when tested by showing the rectangles but not giving any reward. Some record must therefore have been present, and the deficiency of the animals was that their behaviour was controlled, not by the record in the memory, but by the food or shock given shortly before. In particular, after receiving any food they attacked everything, including the figure that had yielded shocks. We might say that the information in the memory was not properly read-out and used to influence behaviour. Further experiments then showed that if the effects of previous food or shock were eliminated, the octopuses without vertical lobes possessed quite effective memory records. This was demonstrated by testing their powers to discriminate between the figures shown simultaneously. It thus became irrelevant whether the tendency to attack was high or low, and it was found that the memory was the deciding factor [7].

The tactile memory system

The information about the actions of the vertical lobes thus gives us various insights into the complexities of the memory process. One of the most interesting features of the situation is that the whole system of circuits is repeated in the second memory system, which establishes a record of the results of information from the tactile and chemoreceptors of the arms (figures 4 and 15). It was shown some time ago [8] that octopuses can learn not to draw in objects of a particular texture. After removal of brain tissue, this capacity remained, at least to some extent, so long as a relatively small number of the small cells in the lower part of the system were intact. The 'auxiliary' circuits associated with the tactile memory are based on exactly the same plan that is found in the visual system, using two pairs of lobes. The same workers showed, moreover, that there are close similarities in function. For example, in animals with injuries to the upper circuit, there is no transfer to the other seven arms if teaching is given to only one arm. If the upper circuit is intact, the other arms all learn.

The learning system for touch may prove to be even more suitable than the visual one for investigation of the changes that occur during learning. The number of cells involved is smaller and they are more accessible to experiment. The region that seems to be responsible for storage contains large cells, with small ones around them (figure 12), but the details of their connections are not known. It is probably worth while to devote every effort to establishing how the tactile information is coded and where it is stored. Intensive investigations of these systems with the electron microscope, with the microelectrode, and by chemical and physical means can perhaps be undertaken here with some hope of finding a definite change as a result of learning.

The origin of learning

The arrangement of these two distinct memory systems suggests how the learning system may have arisen. The two sets of circuits are attached to the ganglia whose nerve cells control the jaws, the radula, and the poison glands, and hence the process of eating. The learning systems are, as it were, developments of the reflex mechanism that decides what is eaten. Like any reflex system, this eating mechanism must be capable of being inhibited. Eating must stop if the food is prickly, corrosive, or otherwise injurious. There is some evidence [9] that inhibition in mammals involves the presence of small nerve cells among the large motor ones. In an octopus, there are inner layers of small cells mixed with the large ones that control the jaws. The very numerous minute cells that are so characteristic of the learning centres form layers that are directly continuous with these small cells of the reflex centres. This suggests that learning is an extension of the process by which reflexes are temporarily inhibited. Indeed, during embryonic development, the learning centres can be seen to differentiate as the upper parts of the lobes concerned with motor functions (figure 17). In the higher centres, the mechanism of 'choice' between reflexes is thus developed to provide a more permanent record. The small cells, which at first served only for temporary inhibition of reflexes, have become specialized so as to produce effects that last perhaps for the lifetime of the animal.

The search for the learning changes

These anatomical studies and learning experiments do not show us exactly how the memory system works. Other interpretations are possible for some of the experiments. However, the observations do provide us

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

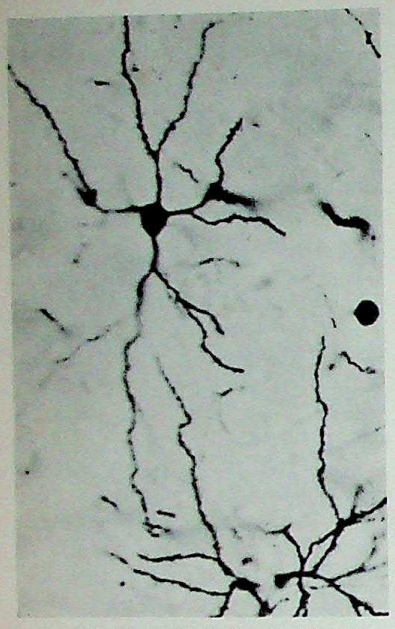


Figure 16 Dendritic fields of cells of the cat's cerebral cortex. Section parallel to the surface (Golgi's method). (By courtesy of Dr M. Colonnier.) (×300)

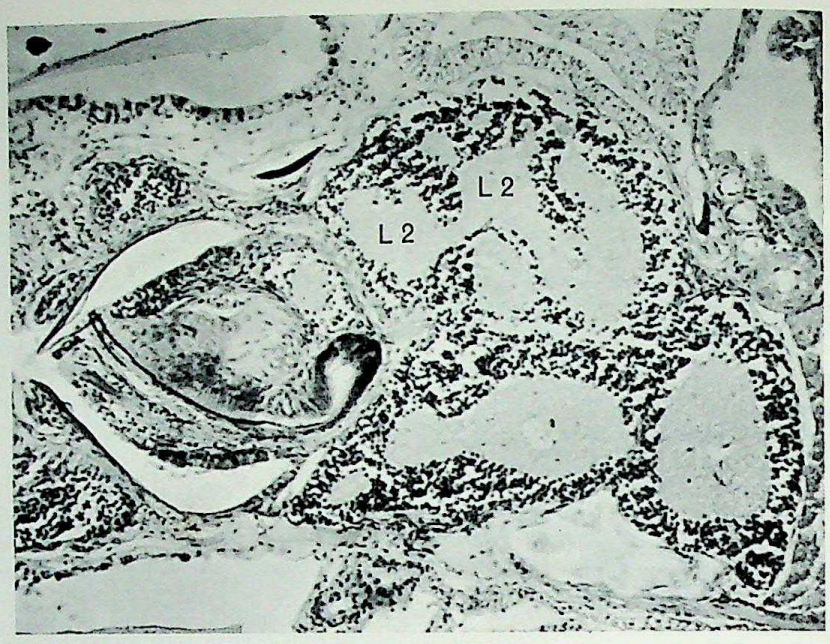


Figure 17 Section through the head of an unhatched octopus. Only the two lower second centres are well differentiated (L_2). In the visual system, the two upper centres can just be seen; in the tactile system, they as yet form only a few cells above the lower lobe. (×160)

with a proof that the small neurons play a key part. They allow the hypothesis that these cells are specialized to produce a change, sudden or gradual, that closes one of two possible outputs from the classifying systems.

These should be useful clues in the search for the changes that occur during learning. It is not always realized that a very specific strategy is needed for this enquiry. Brains contain many parallel channels, and any changes that occur are likely to be spread widely throughout the tissue. Moreover, in any animal that has already learned a lot, it is not likely to be easy to identify the changes that result from learning any single new performance. Many workers have suggested that learning changes are likely to be found at the synaptic junctions, where one nerve cell stimulates or inhibits another. But a single large mammalian cortical neuron may carry up to 30 000 synaptic endings. We should be able to recognize only some very drastic change.

There is some evidence of changes in the base ratios of the ribose nucleotides of nerve cells after training [10]. According to the present interpretation, such changes would not themselves encode the items to be recorded. If there are cells specifically triggered to be able to close one of two pathways it may well be expected that their nucleotides would be involved in the process, and hence changed during it.

Some workers have suggested that learning changes may be similar to those of the 'facilitation' by which trains of impulses come to pass more rapidly through reflex arcs [11]. Others have shown changes during learning in the electrical activity of cells [12]. The learning change indeed probably has several aspects, if only because it requires the co-operation of various distinct activities. There are many difficulties in the problem, which no doubt explains the scant progress so far made. Since the difficulties largely turn on discovering where to look, there is some hope that studies of the connection pattern of systems that are known to learn, such as those of the octopus, may help towards a solution.

Acknowledgments

A great deal is owed to the many who have assisted in the work with *Octopus*, including especially the Director and staff of the Zoological Station at Naples and Mr B. B. Boycott. Mr V. Barber and Mrs M. Nixon kindly helped with the preparation of the article and Mr J. Armstrong, Miss T. Hogan, and Miss P. Stephens with sectioning and photography. The work has been assisted by the Nuffield Foundation and the U.S. Air Force Office of Scientific Research.

References

[1] Sutherland, N. S. *Nature, Lond.*, **179**, 11, 1957.
[2] Young, J. Z. 'A Model of the Brain'. Clarendon Press, Oxford. 1964.
[3] Hebb, D. O. 'The Organisation of Behaviour'. John Wiley & Sons, New York. 1949.
[4] Young, J. Z. *Biol. Rev.*, **36**, 32, 1961.
Idem. Proc. roy. Soc., B, **159**, 565, 1964.
[5] Penfield, W. and Milner, B. A.M.A. *Arch. Neurol. Psychiat.*, **79**, 475, 1958.
[6] Muntz, W. R. A. *J. Comp. physiol. Psychol.*, **54**, 186, 1961.
[7] Muntz, W. R. A., Sutherland, N. S., and Young, J. Z. *J. exp. Biol.*, **39**, 557, 1962.
[8] Wells, M. J. *J. exp. Biol.*, **36**, 590, 1959.
[9] Eccles, J. C. 'The Physiology of Synapses'. Springer-Verlag, Berlin. 1964.
[10] Hydén, H. and Egyhazi, E. *Proc. nat. Acad. Sci., Wash.*, **48**, 1366, 1962.
[11] Eccles, J. C. and McIntyre, A. K. *J. Physiol.*, **121**, 492, 1953.
[12] Morrell, F. In 'Moscow Colloquium on Electroencephalography of Higher Nervous Activity' (H. Jasper and G. D. Smirnov, editors). Moscow. 1960. Jasper, H. H., Ricci, C. F., and Doane, B. In 'Ciba Symposium. Neurological basis of behaviour' (C. E. W. Wolstenholme and C. M. O'Connor, editors). Churchill, London. 1958.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Insect hormones

Digitized by Arya Samaj Foundation Chennai and eGangotri

077823
L 04 E
V. 24
G 3444

Sir Vincent B. Wigglesworth

In recent years, a wide range of insect hormones has been identified by their physiological action, and some have been characterized chemically. Increasingly, it is becoming clear that there is no sharp distinction between the endocrine organs and the nervous system, and that the latter plays an essential role in the formation and liberation of the secretions that regulate the metabolism.

The earliest hormones to be recognized in vertebrates were those derived from the interstitial cells of the testis, which are responsible for the regulation of the secondary sexual characters. Castrations of young insects, and transplantations of the testes and ovaries into the opposite sex, were carried out by a number of investigators at the turn of the century, but such experiments gave uniformly negative results. This particular type of hormone action does not appear to operate in insects.

Nevertheless, during the past fifty years, and particularly during the past ten years, it has become evident that hormones of many sorts are concerned in regulating the growth and form of insects and in influencing many aspects of their metabolism and behaviour. This article conveys some idea of the number and variety of these insect hormones and of the central part played by the nervous system in their production.

It is confusing and misleading to compare the hormone system of insects in detail with that of mammals, but in spite of this there are many obvious points of similarity between the two. The most important of these are the following:

1. In both there are neurohumours: these are pharmacologically active metabolites liberated from the endings of the neurones.
2. There are ductless glands in both. In insects, these consist of cell nests that have been budded off from the ectoderm at an early stage of development and carried inwards to form discrete endocrine organs comparable with the thyroid gland or the glandular part of the pituitary in mammals.
3. In both there are specialized neurones whose cell bodies contain stainable inclusions that are carried along the axons before being set free into the circulating blood. These are the so-called neurosecretory cells. The clumps of material that accumulate in their cytoplasm take up the same, more or less specific, stains in mammals and in insects; when examined with the electron microscope, these clumps are seen to be made up of spheres, 1000–3000 Å in diameter, that are opaque to electrons.
4. In insects, as in vertebrates, the product of the neurosecretory cells is often conducted to a specific organ, such as the neurohypophysis of vertebrates, which serves as a gateway for the escape of the active principle from the neurones to the circulating blood. Organs of this kind were first recognized in Crustacea and have been named neurohaemal organs by F. Knowles [1].

There are four principal components in the endocrine system of insects, namely the endocrine glands, the neurosecretory cells, the neurohaemal organs, and the neurohumours. Briefly, these have the following characteristics.

The endocrine glands. The ductless glands of insects arise during embryonic development from clusters of ectodermal cells at the base of the mouth parts; these clusters later get carried backwards into the head and thorax. When they come to rest in the head they are called ventral glands—they are in the ventral part of the head; often they are carried further back, and are then termed thoracic or prothoracic glands. The prothoracic glands of the caterpillar were well described by P. Lyonet as early as 1762 in his classic work on the goat moth caterpillar (figure 1) [2]. Lyonet even proposed a possible function for these organs and carried out some experiments to test his idea. They proved negative, and he concluded by saying that it would be necessary to follow the fate of the glands in the chrysalis and in the moth in order to discover their true function. That task has required nearly two hundred years.

Other glands that arise in the same way come to rest behind the brain, in close association with the sympathetic nervous system; these become the corpora allata, which are among the most important endocrine organs in insects. As their name implies, these bodies are commonly paired and laterally placed; but in some insects (figure 3) they fuse during development to form a single structure in the mid-line.

The neurosecretory cells. These are recognizable by their characteristic staining properties (figure 2) and by their bluish appearance under dark-ground illumination, which results from the scattering of light by the fine particles that compose the secretory product. They are present in all the ganglia, from the brain and suboesophageal ganglia in the head to the last ganglion in the abdominal chain.

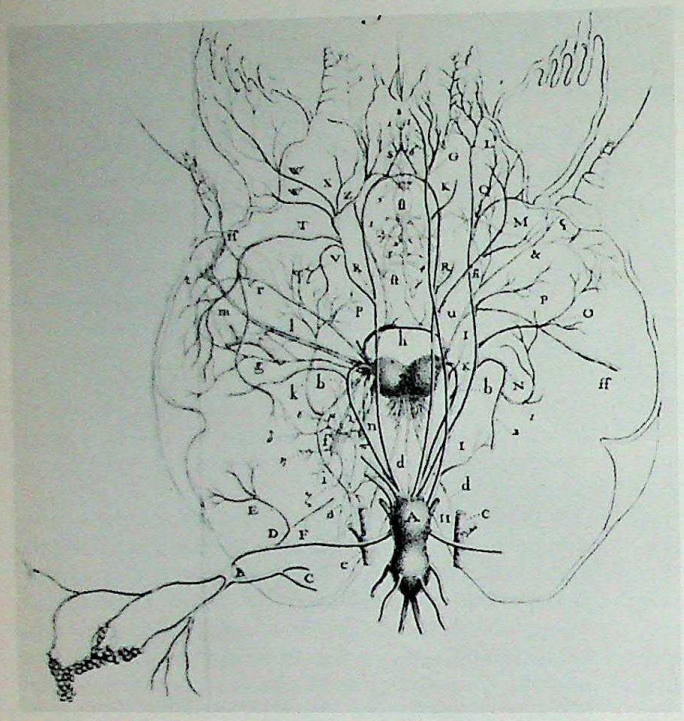
Neurohaemal organs. The best known of these are the corpora cardiaca. The corpus cardiacum of each side lies just behind the brain, in close association with the corresponding corpus allatum. They are organs of nervous origin, made up of three components. These are, firstly, the bulbous endings of the axons of neurosecretory cells located in the dorsum of the brain, which commonly contain masses of stored neurosecretory material; secondly, secretory cells of nervous origin with axon-like processes running into the nerves supplying the heart and other organs; and, thirdly, glial cells wrapped around the cells and axons [3].

Neurohumours. These can be extracted from the brain and other ganglia. Their precise origin is uncertain.

Sir Vincent Wigglesworth, *C.B.E., M.D., F.R.S.*
Was born in Lancashire in 1899 and educated at Repton School, Cambridge University, and St Thomas's Hospital, London. In 1926 he was appointed Lecturer, and subsequently Reader, in medical entomology at the London School of Hygiene and Tropical Medicine, and so began a lifelong study of insect physiology. In 1943 he was made Director of the Agricultural Research Council's unit of insect physiology and in 1945 he returned to Cambridge as Reader in Entomology. Since 1952 has been Quick Professor of Biology.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri



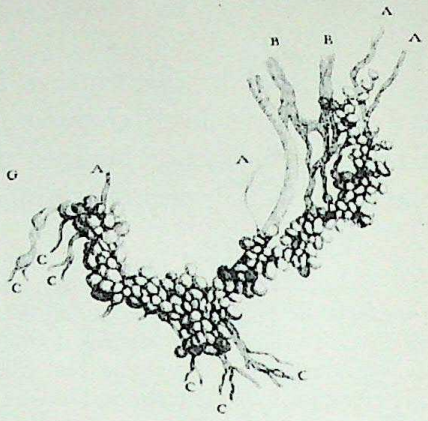


Figure 1 Dissections of the goat moth caterpillar by Lyonet [2], showing the *vaisseaux grenus* (bottom left), now recognized as the prothoracic gland, shown in detail above. (Same size as Lyonet's illustration.)

Figure 2 Section of the brain of *Rhodnius*, showing the large neurosecretory cells deeply stained.

Hormones in growth and diapause

The medial group of neurosecretory cells in the dorsum of the brain is the source of the hormone that initiates growth and moulting in insects. The axons from these large lobulated cells cross over and run to the corpus cardiacum of the opposite side, where their product is believed to be set free into the circulating blood. It thus reaches the thoracic glands (or the ventral glands of the head) and induces these to secrete the hormone that initiates growth in the epidermal cells, leading on to the deposition of the new cuticle in readiness for the moulting of the old (figure 3).

The effective stimulus to the neurosecretory cells differs in different insects. In the blood-sucking bug *Rhodnius*, the distension of the abdomen by the meal of blood provides a nervous stimulus to the brain [4]. In locusts, the act of chewing and swallowing seems to provide the stimulus [5].

The conclusion that the brain is the source of a hormone necessary for the pupation of caterpillars was reached by S. Kopeč in 1917. Tracing the source to the neurosecretory cells came more than twenty years later [6]; this was the first demonstration of a definite function for the neurosecretory cells in any animal.

The chemical nature of the brain hormone is still uncertain, but the hormone of the thoracic gland has been isolated in crystalline form. It appears to be a steroid, which can occur in several chemical variants; experiments with labelled material show that cholesterol injected into the insect can be converted into it [7].

Many insects are subject to periods of arrested growth (diapause) which commonly supervene during hibernation. The immediate cause of the arrest is usually a failure of the brain to secrete the hormone that activates the thoracic gland. In the dormant state, the epidermal cells are attenuated and contain few mitochondria. On exposure to the moulting hormone, nucleic acid is formed and the mitochondria increase in number; protein synthesis and growth are thus restored [8–10].

In some insects, notably in the Diptera *Chironomus* and *Drosophila* which have giant chromosomes in the salivary glands and other cells, these synthetic processes are preceded by the activation or 'puffing' of certain specific loci in the chromosomes. It looks as though the hormone may be exerting its action in the first instance on the chromosomes themselves [11].

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

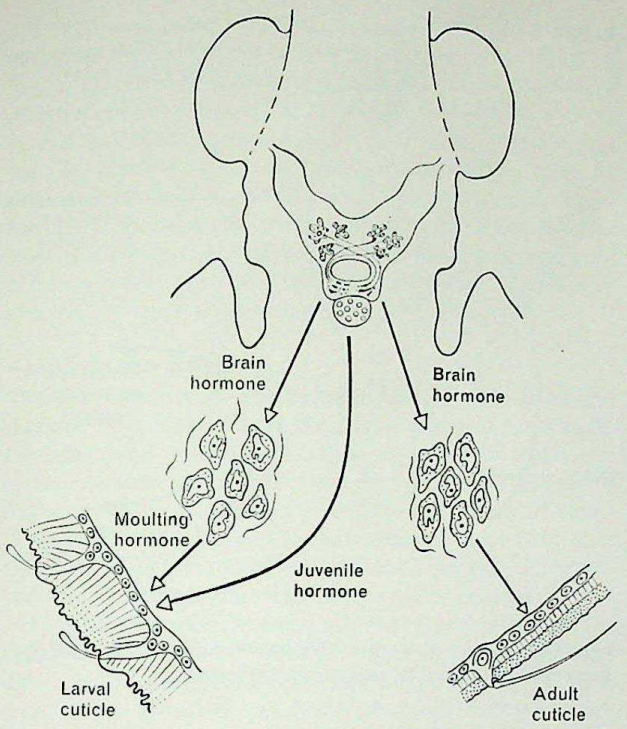


Figure 3 The glands of internal secretion and the hormones controlling growth and metamorphosis (*Rhodnius*). The brain at the back of the head contains neurosecretory cells, the axons from which end in the corpus cardiacum, where the brain hormone is set free into the blood. This acts on the thoracic gland, causing it to secrete the moulting hormone. When the moulting hormone alone acts on the epidermal cells (right), these cells during moulting produce an adult type of cuticle. But when the moulting hormone acts in the presence of the juvenile hormone, secreted by the corpus allatum lying just behind the corpus cardiacum, the epidermal cells (left) produce a larval type of cuticle.

Hormones and the control of form

The form of any animal is dependent on the activity of particular sets of genes. In insects, several gene outfits seem to have been differentiated within each species, and these are capable of being brought into action at different stages of the life cycle and thus lead to the appearance of the larva, the pupa, and the adult insect.

The activity of these partially separable gene systems is regulated by the presence or absence of the hormone secreted by the corpus allatum, which is commonly called the juvenile hormone. For example, when the epidermal cells of *Rhodnius*—in insects whose growth and moulting have been set going by the moulting hormone—are exposed to the juvenile hormone, they lay down cuticle of larval type. If the juvenile hormone is absent, the epidermal cells undergo the exaggerated growth necessary to produce wings and external genitalia and lay down cuticle of adult type (figure 3).

The immediate cause of metamorphosis in the insect is the arrest of secretion of juvenile hormone by the corpus allatum; this arrest is regulated by nervous control from the brain [12]. Whether the control is effected by nerve impulses or by neurosecretory material is uncertain. The intermediate type, the pupa, is produced when there is a very small amount of juvenile hormone circulating in the blood [13] (figure 4).

Metamorphosis is an example of an animal changing its form in the course of its life cycle. In addition, many insects provide examples of polymorphism affecting different individuals. These differences in form are genetically determined, but in many instances the genetic switch—that is, the activation of the alternative set of genes—is brought about by changes in the environment. There is evidence that in some cases the agent immediately involved in the switch is hormonal, and may indeed sometimes be the juvenile hormone itself. This seems to be so in the winged and wingless forms of aphids and in the solitary and gregarious forms of locusts [14].

Substances with juvenile hormone activity have been extracted from a wide variety of sources in the animal and plant kingdoms. They have been obtained from all the insects studied; from many other invertebrates; from the suprarenal glands and many other organs in vertebrates including man; and from higher plants, yeasts, and some protozoa and bacteria [15]. Where the chemical nature of these substances has been explored they have proved to be a mixture of farnesol and farnesal [16]. Farnesol is an unsaturated primary alcohol having the formula $(CH_3)_2C{:}CH.CH_2.CH_2.C(CH_3){:}CH.CH_2.CH_2.C(CH_3){:}CH.CH_2OH$; farnesal is the corresponding aldehyde. These same isoprenoid derivatives seem to be the active components in the natural hormone in the insect, although here, perhaps, they may normally be present in combination with protein or some other large carrier molecule [17].

Farnesol formation is an intermediate step in the biosynthesis of cholesterol and carotene [18]. Insects cannot synthesize these materials, but given labelled mevalonic acid they can synthesize labelled farnesol and farnesal, showing the usual juvenile hormone activity [19].

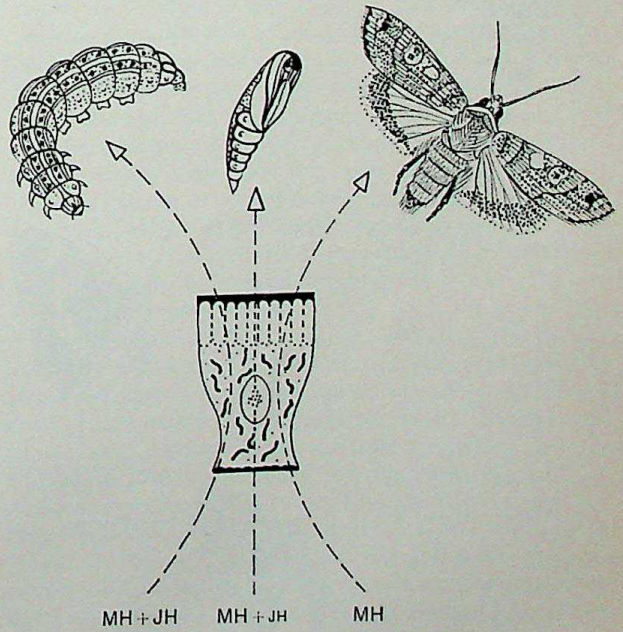


Figure 4 Illustration of control of metamorphosis in, for example, Lepidoptera, by means of hormones. When the epidermal cells are exposed to moulting hormone (MH) plus a large amount of juvenile hormone (JH), the larval form is produced on moulting. When moulting hormone plus a trace of juvenile hormone is present, the pupal form appears. When moulting hormone alone is acting, the adult moth develops.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Hormones and reproduction

The neurosecretory cells in the dorsum of the brain, and the corpus allatum itself are concerned in reproduction. In adult locusts, the product of the neurosecretory cells in the brain appears to act upon the cells of the fat body (roughly equivalent to the liver of vertebrates) and causes these to synthesize the blood proteins that are taken up by the ovaries to form the yolk of the developing eggs. The corpus allatum resumes its secretory activity in the adult insect. The juvenile hormone which it secretes is at this stage necessary, in most insects, for the activation of yolk deposition in the female and for the formation of the sperm packets (spermatophores) that are necessary for mating in the male. The same substance appears to be concerned in controlling metamorphosis in the young stages and in inducing yolk formation in the adult: farnesol will induce the ripening of eggs in *Rhodnius* deprived of the corpus allatum [17].

Certain insects enter a state of diapause in the adult stage. This takes the form of an arrest of reproduction in the adult female, and—in some instances at least—it results from the cessation of juvenile hormone secretion by the corpus allatum. This happens, for example, in the Colorado potato beetle *Leptinotarsa*. In the autumn, this beetle burrows into the soil; there it becomes immobile, the eggs no longer mature, the rate of metabolism falls, and the thoracic muscles degenerate. If active corpora allata are implanted into these hibernating beetles, all these changes are reversed [20].

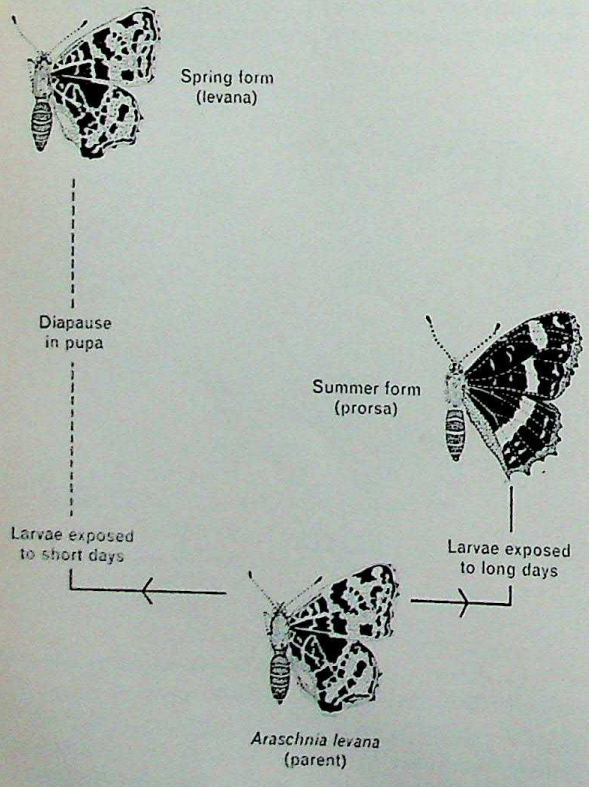


Figure 5 Control of diapause and the appearance of spring (levana) and summer (prorsa) forms in the butterfly *Araschnia levana* by regulating the photoperiod during the life of the caterpillar.

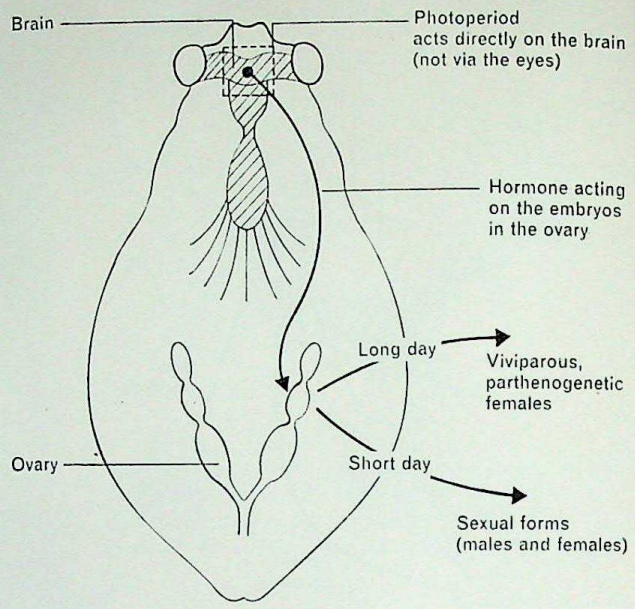


Figure 6 Control of reproductive polymorphism in the pea and bean aphid *Megoura* by regulating day-length.

Hormones and diapause in the silkworm egg

In those races of the domesticated silkworm that have two generations in one year, the eggs of the second generation enter a state of dormancy that persists throughout the winter. Female moths that are the product of eggs deposited in the summer months lay dormant eggs. The high temperatures, and particularly the long hours of daylight, to which these summer eggs are subjected appear to be the main factors causing dormancy in the eggs of the generation of moths that hatches from them.

The immediate cause of the dormancy is a hormone, produced by neurosecretory cells in the suboesophageal ganglion of the adult female,which acts upon the eggs in the ovaries. It is the past history of the mother, when she was herself an egg or a very young larva, which determines in some unknown way whether the hormone will be released or retained [21].

Delayed action of hormones

The determination of diapause in the egg of the silkworm is an example of the long delay which may sometimes occur between the effective stimulus and its demonstrable effect. It seems likely that in this case the initial stimulus—that is, the length of day to which the egg of the preceding generation was exposed—itself produces some chemical change that exerts a hormonal action on the body and influences its subsequent development.

There are many other examples of this type of delayed action. The length of day to which young larvae are exposed will determine whether or not their pupae later go into diapause. In some butterflies, notably the Nymphalid *Araschnia levana*, not only is the incidence of pupal diapause controlled in this way, but diapausing pupae eventually give rise to the spring variety of the butterfly (the levana form). Non-diapausing pupae give rise to the summer variety (the prorsa form), which is so strikingly different in appearance that it was originally believed to be a separate species [22] (figure 5).

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Certain aphids, such as the pea and bean aphid *Megoura*, if they are exposed to a long day exceeding 14 hours, give rise to female offspring which are parthenogenetic and viviparous. If they are exposed to a short day of less than 14 hours, they give birth to male and female offspring which ultimately mate and lay eggs. In this case, the light enters the head and acts directly upon the brain. The duration of illumination presumably controls the production of a hormone that acts upon the embryos while they are developing in the ovaries and determines their subsequent fate [23] (figure 6).

Hormones and metabolism

The hormones from the neurosecretory cells, from the thoracic glands, and from the corpora allata, have striking effects on metabolism. One or other of them can affect the secretion of digestive enzymes and the rate of digestion in the alimentary canal, the rate of protein synthesis in the fat body and accumulation of proteins in the blood, and the overall consumption of oxygen. They are therefore often spoken of as metabolic hormones.

In many instances, these changes in metabolism are the result of feed-back effects from other physiological processes set in motion by the hormones. It may be that most of the so-called metabolic effects of the insect hormones are homeostatic effects of this kind. It is often difficult to distinguish between direct and indirect effects on metabolism [24].

There are, however, two established examples of hormones which do act directly upon the fat body and control its synthetic activities. Firstly, a hormone from the corpus cardiacum of the cockroach *Periplaneta* brings about a rapid rise in the level of trehalose (the chief sugar of insects) in the circulating blood; it does this by exerting its action on the enzyme system in the fat body where glycogen is stored [25]. Secondly, the juvenile hormone from the corpus allatum of adult *Rhodnius* induces the fat body to synthesize and liberate into the circulating blood the specific proteins which are taken up by the ovaries to be stored in the yolk of the developing eggs [26].

Hormones and diurnal cycles of activity

Insects, like most other living organisms, show cycles of activity which follow an approximately diurnal rhythm and which may often persist for a time even in conditions in which there is no daily cycle of change in illumination or temperature.

A rhythm of locomotion and feeding activity of this kind occurs in the cockroach *Periplaneta*. Janet Harker showed that the nocturnal phase of activity is brought about by a hormone that is circulating in the blood. This hormone is secreted by a group of neurosecretory cells located in the suboesophageal ganglion. The group of cells can be plausibly described as the internal 'clock' of the cockroach; if they are taken from one cockroach with a diurnal rhythm of activity and implanted into the abdomen of a second cockroach which has no rhythm, this second cockroach acquires the rhythm of the first [27].

The clock is set by means of the diurnal cycle of light and darkness, which is perceived through the small simple eyes or ocelli. The stimulus acts indirectly upon the corpus cardiacum and causes this to transmit a neurosecretory stimulus along the nerve running to the suboesophageal ganglion (figure 7).

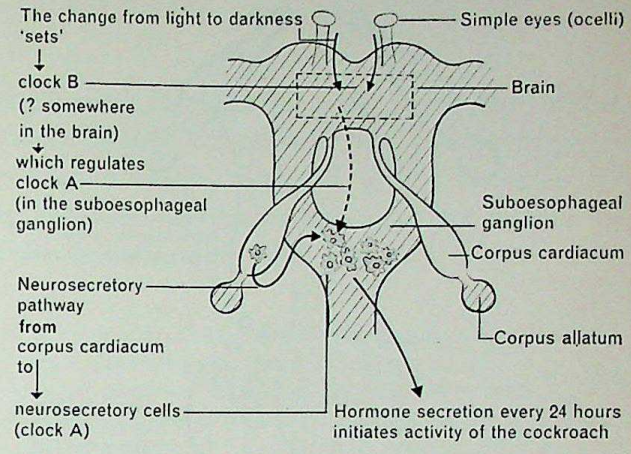


Figure 7 Diagram showing the neurosecretory cells which form the 'clock' of the cockroach, and the setting of this clock by the stimuli received by the ocelli.

This account of the clock system of the cockroach is a greatly simplified one. Other clocks appear to exist in other tissues, and these timepieces influence one another. Moreover, there is a parallel rhythm of growth and cellular activity in the epithelium of the gut which is associated with the diurnal cycle of feeding. If, under experimental conditions, the gut is exposed to two cycles of hormone secretion per day, excessive growth in the gut wall takes place and leads to malignant cancerous tumours which invade the surrounding tissues [28].

Hormones and the control of specific activities

Various activities that take place in the general epidermis of the insect are synchronized throughout the body, and cannot be brought about by nerve impulses to the cells because these are not innervated. They must therefore be controlled by hormones circulating in the blood. Examples are the migration of pigment granules within the epidermal cells of stick insects, which brings about striking changes in colour adapted to the background; the hardening and darkening of the cuticle which take place under the action of the epidermal cells soon after moulting, when the old cuticle has been shed; and the absorption of water from the tracheae after moulting, or hatching from the egg, which leads to the filling of the tracheal system with air.

Other hormonal stimuli affect particular organs. For example, extracts from the corpus cardiacum cause an increased rate and amplitude of the heart-beat and exaggerated muscular contractions of the Malpighian tubules [29]. Again, a hormone from the brain, perhaps from the neurosecretory cells, induces the hardening and darkening of the cuticle of the blowfly after emergence from the pupa [30]. A hormone of unknown origin leads to the breakdown of the thoracic gland in *Rhodnius* within twenty-four hours after metamorphosis to the adult stage, so that further moulting becomes impossible [31]. The neurosecretory cells in the thoracic ganglia of *Rhodnius* secrete a diuretic hormone which stimulates the Malpighian tubules into secreting a copious watery urine [32]. A secretion from the accessory glands of male insects acts upon the genital tract of the female and sets up active peristaltic contractions which carry the spermatozoa upwards to the spermathecae [33].

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

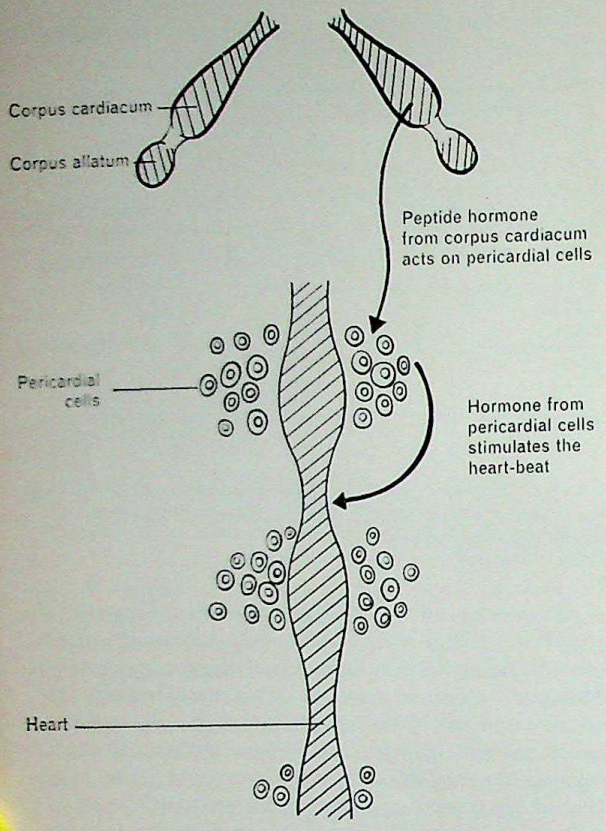


Figure 8 Diagram showing the indirect control of the heart-beat of the cockroach *Periplaneta* by the hormone from the corpus cardiacum.

The above examples are only a few among many. A little more may be said about the stimulation of the heart by the corpus cardiacum. The agent concerned appears to be a peptide hormone, probably secreted by the intrinsic cells of the corpus cardiacum. This hormone does not act directly upon the heart muscle but upon groups of mesodermal cells scattered along the heart, the so-called pericardial cells [34]. When the pericardial cells are exposed to the peptide hormone they quickly become vacuolated and their contents stain with ammoniacal silver. They then set free the active principle which is responsible for stimulating the muscles of the heart (figure 8). The nature of the active substance is not established with certainty. It may be an indolalkyl amine similar to serotonin (although it is not serotonin itself) and is perhaps identical with the active substance from the accessory glands of the male insect which induces peristalsis in the genital tract of the female. This represents an interesting type of hormone action, in which the hormone acts upon some peripheral organ which then liberates the physiologically active substance that brings about the desired effect [34].

Pharmacologically active substances of many kinds can be extracted from the central nervous system of insects. Acetylcholine is always present in exceptionally large amounts. Serotonin (5-hydroxytryptamine) has been reported [35]. A series of neurohumours has been characterized [36]. What is uncertain is whether any of these substances is set free into the blood in the normal insect and whether indeed they exert any physiological action during life.

Conclusion

The way in which insect hormones have been discussed in this article was deliberately chosen to bring out an important general conclusion. In some ways it would have been more enlightening to select a single example and to examine this in greater detail. To have done so would, however, have obscured a generalization that becomes apparent when the whole picture is considered, even as cursorily as has been necessary here. It becomes more and more obvious that there is no sharp line of distinction between the endocrine organs and the nervous system. More and more of the processes of the body are seen to be controlled by means of chemical messages, and the central nervous system is seen to play a role in the formation and liberation of these regulatory secretions which rivals in importance the control of activity by means of electrical impulses conducted along the nerve fibres. The wheel has come full circle, and the cerebral humours of old, which were supposedly discredited in the nineteenth century, are coming into their own. Again and again, these hormones are being found to exert their effects by suppressing or evoking particular activities that are latent in the gene system.

References

[1] Carlisle, D. B. and Knowles, F. 'Endocrine control in crustaceans'. University Press, Cambridge. 1959.
[2] Lyonet, P. 'Traité anatomique de la chenille, qui ronge le bois de saule', 1762.
[3] Scharrer, B. *Z. Zellforsch.*, 60, 761, 1963.
[4] Wigglesworth, V. B. *Quart. J. micr. Sci.*, 77, 191, 1934.
[5] Clarke, K. U. and Langley, P. A. *J. insect Physiol.*, 9, 287, 1963.
[6] Wigglesworth, V. B. *J. exp. Biol.*, 17, 201, 1940.
[7] Karlson, P. *Angew. Chem.*, Internat. edit., 2, 175, 1963.
[8] Wigglesworth, V. B. *Symp. Soc. exp. Biol.*, 11, 204, 1957.
[9] *Idem. J. exp. Biol.*, 40, 231, 1963.
[10] Telfer, W. H. and Williams, C. M. *J. insect Physiol.*, 5, 61, 1960.
[11] Clever, U. *Devel. Biol.*, 6, 73, 1963.
[12] Wigglesworth, V. B. 'The physiology of insect metamorphosis'. University Press, Cambridge. 1954.
[13] Piepho, H. *Verh. dtsch. zool. Ges.*, 62, 1951.
[14] Kennedy, J. S. (Editor). 'Insect polymorphism'. *Symp. Roy. ent. Soc. Lond.*, 1, 1961.
[15] Gilbert, L. I. and Schneiderman, H. A. *Trans. Amer. micr. Soc.*, 79, 38, 1960.
[16] Schmialek, P. *Z. Naturforsch.*, 16b, 461, 1961.
[17] Wigglesworth, V. B. *J. insect Physiol.*, 9, 105, 1963.
[18] Wagner, A. F. and Folkers, K. *Endeavour*, 20, 177, 1961.
[19] Schmialek, P. *Z. Naturforsch.*, 18b, 462, 1963.
[20] Wilde, J. de. *A. Rev. Ent.*, 7, 1, 1962.
[21] Hasegawa, K. *Nature, Lond.*, 179, 1300, 1957.
[22] Müller, H. J. *Naturwissenschaften*, 42, 134, 1955.
[23] Lees, A. D. *J. exp. Biol.*, 41, 119, 1964.
[24] Wigglesworth, V. B. *Adv. insect Physiol.*, 2, 247, 1964.
[25] Steele, J. E. *Gen. comp. Endocrin.*, 3, 46, 1963.
[26] Coles, G. C. *Nature, Lond.*, 203, 323, 1964.
[27] Harker, J. E. 'The physiology of diurnal rhythms'. University Press, Cambridge. 1964.
[28] *Idem. J. exp. Biol.*, 35, 251, 1958.
[29] Cameron, M. L. *Nature, Lond.*, 172, 349, 1953.
[30] Cottrell, C. B. *Adv. insect Physiol.*, 2, 175, 1964.
[31] Wigglesworth, V. B. *J. exp. Biol.*, 32, 485, 1955.
[32] Maddrell, S. H. P. *Ibid.*, 40, 247, 1963.
[33] Davey, K. G. *Can. J. Zool.*, 38, 39, 1960.
[34] *Idem. Gen. comp. Endocrinol.*, 1, 24, 1961.
[35] Colhoun, E. H. *Adv. insect Physiol.*, 1, 1, 1963.
[36] Gersch, M. *et al. Z. Naturforsch.*, 15b, 319, 1960.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Cell movements

Digitized by Arya Samaj Foundation Chennai and eGangotri

E. J. Ambrose

It is possible to observe a continuous movement in the cytoplasm of cells, and it now seems likely that the cytoplasm is driven by forces that originate at or near the cell membrane. These forces may be either mechanical or electrical in origin, and this article discusses the evidence for each of the two possibilities. It also considers the hypothesis that the movement of whole cells, particularly mammalian tissue cells, is connected with that of the cytoplasm.

Research on the movements of cells is less well known and on a much smaller scale than is research into molecular biology. This is partly because the problem is more complex, as it is necessary to work with whole cells. Damage to a cell causes it to lose most of its motility, whereas protein synthesis and nucleic-acid studies can be carried out using disrupted cells. But there have been some interesting developments in recent years which are summarized in this article. The subject can be divided broadly into two sections, internal movements of the cytoplasm within the cell, and the locomotion of whole cells. I hope to be able to show that these two activities are to a certain extent interrelated.

Movements of the cytoplasm

When a cell is examined under the highest power of the light microscope, granules in the cytoplasm can be seen to be in continuous movement. This movement is in the region known as the endoplasm or sol, in contrast to the ectoplasm or cortical gel which can be observed in some cells as a thin layer near the wall. Part of this movement is Brownian movement due to thermal agitation, but much of it cannot be explained in this way—the cytoplasm flows continuously in many cases, particularly in plant cells. Time-lapse films of animal cells in culture also show local regions of streaming within the cell, and many protozoa exhibit large-scale streaming during locomotion. In figure 9 is shown a photograph of a young apical cell of the alga *Chara*. The cell contains cytoplasm surrounding a large central vacuole and the cytoplasm flows continuously round the wall. The rows of chloroplasts embedded in the wall can be clearly seen in this photograph. The rate of flow can be very high, reaching a velocity of 60μ per sec in mature internodal cells. Streaming in these cells has been the subject of some beautiful experiments by Japanese botanists, particularly by N. Kamiya, K. Kuroda, and T. Hayashi. The central vacuole can be removed in a centrifuge so that the cell is filled with protoplasm; the velocity of streaming can then be measured through the whole depth of the cell. The maximum velocity is found to occur adjacent to the cell wall [2] (figure 1). Similar results can be obtained with other plant cells. However, the rhizoids of *Chara* contain quite small cells in which the layer of cytoplasm is so thin that the change of velocity with depth cannot be measured. E. J. Ambrose and R. J. Goldacre observed the movements after the cytoplasm had been thickened somewhat by treatment with neutral red (figure 2). Particles reaching the end of a region of rapid streaming, *A*, tend to overshoot and are then carried passively round the region *B*. On reaching the cell wall on the other side, the particles begin to move again on their own and rapidly acquire their original velocity.

Another experiment on cytoplasmic movement is illustrated in figure 3. A large internodal cell is suspended in a saline medium with a salt concentration similar to that of cytoplasm. The cell is maintained under slight hydrostatic pressure and the end cut off. Cytoplasm will now flow up the left-hand wall and down the right-hand wall of the cell. This will continue for as long as half an hour, and a pool will collect in the bottom of the dish. In the pool, where there is no cell wall, there is no general streaming of cytoplasm, although small-scale movements of organelles continue. These and various other experiments have provided good evidence to show that the driving force for streaming in plant cells originates at the contact between the endoplasm and the cell membrane with its associated ectoplasm.

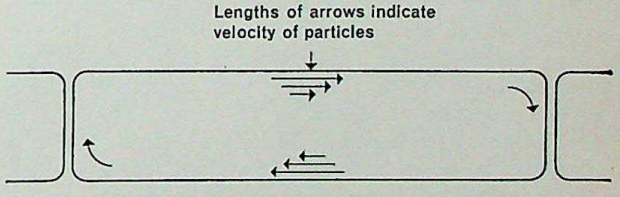


Figure 1

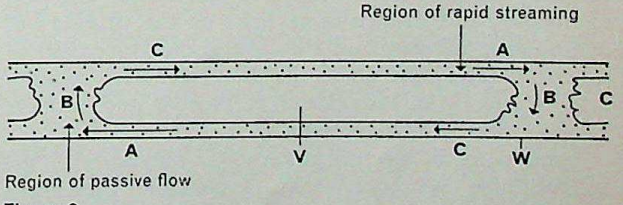


Figure 2

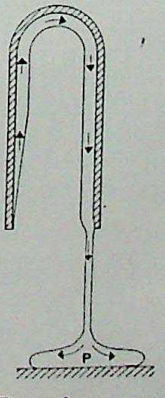


Figure 3

Figure 1 Speed of streaming in internodal cell of *Chara*. The arrows indicate the relative velocities of granules.

Figure 2 Streaming in the rhizoid of *Chara* after treatment with neutral red. Arrows indicate velocities. *A*, region of streaming; *C*, region of increasing rate of streaming; *B*, return flow; *V*, central vacuole; *W*, cell wall and cell membrane.

Figure 3 *Nitella* cell mounted in balanced saline with lower end removed. Arrows show direction of streaming. *P*, pool of cytoplasm.

E. J. Ambrose, *M.A., D.Sc.*
Was born in Cambridge in 1914 and educated at Cambridge University. After war-time research with the Admiralty, he entered the field of research on protein structure. During the last twelve years he has been studying the properties of cancer cells at the Institute of Cancer Research in London, where he is Reader in Physical Chemistry.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

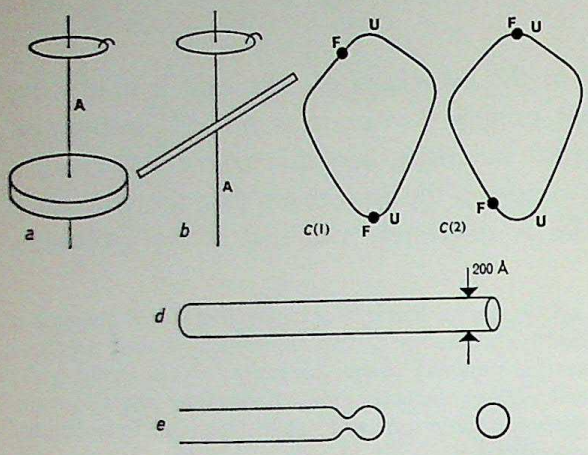


Figure 4 *(a)*, Spinning isolated chloroplast; A, axis of rotation; *(b)*, rotating fibril; A, axis of rotation; *(c)*, hollow polygon of fibrils; F, fixed granules on fibrils; U, undulation travelling round fibril; 1,2, successive intervals of time; *(d)*, shape of a microtubule; *(e)*, formulation of a microtubule from a membranous sheet.

There is another kind of continuous movement in cytoplasm. Embedded in the cell wall of *Chara* cells are chloroplasts, the organelles that contain chlorophyll and are the centres of photosynthesis. Occasionally one of these will break away from the wall, and it will then rotate about its own axis in the cytoplasm (figure 4a). These rotating chloroplasts, as well as rotating nuclei, can also be seen in the pool of cytoplasm which collects in the dish shown in figure 3. In addition, there are small tubules which can just be resolved in the light microscope, and are seen to rotate rapidly (figure 4b) [1]. When dispersed with a microneedle, these tubules continue to rotate rapidly, but they soon aggregate to form hollow polygons as shown in figure 4c. The rate of rotation now decreases, but the hollow polygon begins to undulate, as shown in figures 4c and 4d. These undulations travel round the polygon without any striking movement of the granules attached to the fibrils. Electron microscopy has thrown more light on the structure of cytoplasmic tubules, and they are known to consist of microtubules about 200 Å in diameter. The rotating tubules seen by R. Jarosch and K. Kuroda are probably bundles of these microtubules.

Some work in electron microscopy suggests that the microtubules originate from cytoplasmic membrane sheets, endoplasmic reticulum or the centrioles. They are also present in the mitotic spindle. The so-called spindle fibres also consist of microtubules; tubules are also localized near to internal surfaces of the resting cell. They are embedded in parallel array at the surface of the cortical gel near the cell wall and are probably similarly localized on chloroplasts and nuclear membranes. A key to understanding their properties probably provides the key to understanding cytoplasmic movements in general.

The driving force for cytoplasmic movement

Let us now consider the possible nature of the driving force for cytoplasmic movements in plant cells. Experiments such as that shown in figure 3 indicate that hydrostatic pressure within the cell cannot be responsible. The motive force is local and lies on or near the cell membrane. Kamiya [2] found that the movement, cyclosis, was dependent upon adenosine triphosphate, and this led him to suggest that there might be contractile proteins localized near the cell membrane which were in some way responsible for the movement. Jarosch has postulated that winding and unwinding of helical molecules might provide the triggering action—the flow of water produced by the beating of cilia, bacterial flagella, and the spiral beating of sperm tails is well known. However, the evidence seems against this. According to the experiments of Kuroda, using isolated cytoplasm, the separated fibrils rotated extremely rapidly, but when they aggregated to form bundles they began to undulate, and the rate of rotation was much reduced. Again, cilia and flagella drive water by beating, and execute quite complicated movements in which the cilia lie at right angles to their surface of attachment at one stage, but the microtubules are embedded in the cortical gel and lie parallel to the surface. Finally, cilia have an organized structure, consisting of a hollow tube with nine fibres inside and two in the centre, which is not seen in the microtubules.

It is distinctly possible that the actual motive force may not be mechanical at all, and Ambrose and Goldacre suggest [4] that it might be electrical—Faraday had once proposed the same idea. If we bear in mind the evidence that cyclosis depends on ATP, it is interesting to note that the active transport of ions through membranes also depends on phosphate-containing molecules as sources of energy. This transport produces electrical potentials across the cell membrane. In some cells these potentials are very high—in *Chara* they reach 140 millivolts. Now there is an electrical force, electro-osmosis, that can drive water parallel to a surface. The experiment illustrated in figure 5 demonstrates this. A glass tube is packed with glass wool in the region A and reversible silver/silver chloride electrodes are placed in the side arms. If a potential difference of about 100 volts is applied across the electrodes, water will flow continuously round the tube in a circular path as shown by the arrow. The flow is produced by electro-osmosis at the surface of the glass wool. Figure 6 illustrates the mechanism. There are electrical charges on almost any surface; on glass

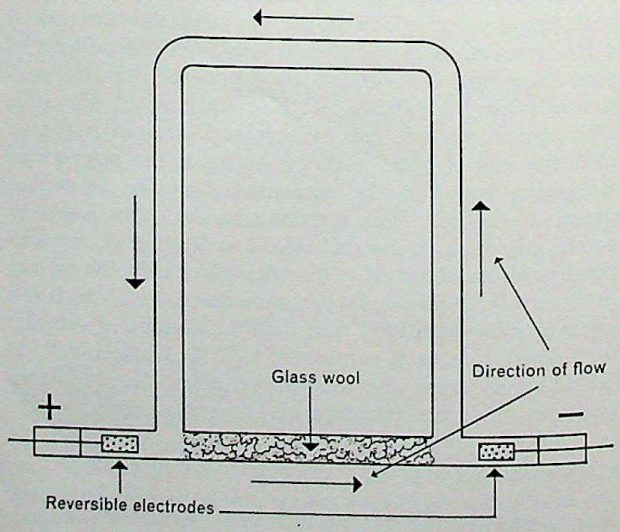


Figure 5 Glass model to produce rotation of water by electro-osmosis. Arrows indicate direction of flow.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

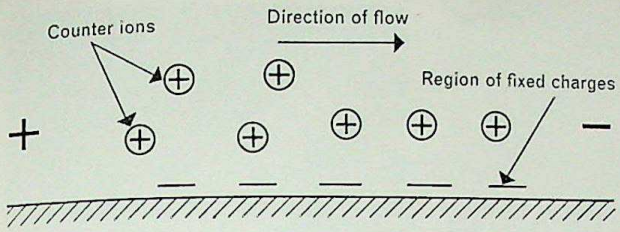


Figure 6 Electro-osmosis at a charged surface. Fixed negative charge on the surface, moving positive ions.

they are due mainly to silicate groups. On cell membranes they may be due to phospholipid ($\rightarrow P\bar{O}$) or acid polysaccharide groups. When such a surface is placed in a salt solution, the oppositely charged ions of sodium or potassium are attracted to the surface, where they form a diffuse double layer. If an electrical potential exists parallel to the surface, the double layer of positive ions will move towards the cathode. Because each ion carries a shell of bound water, the whole layer of water moves along the surface. For electro-osmosis to occur at the surface of a cellular membrane, it is necessary only that a potential difference should exist along, rather than through, its surface. Large potential differences certainly exist across cell membranes, and if a leak or breakdown occurs in the structure, this will produce a variation of potential along the surface. The structure shown in figure 7 has been proposed by Ambrose and Goldacre. Adjacent to the region of pumping pores is a region of membrane leaks; circular currents will flow as shown. The membrane is extremely thin ($\sim$70 Å) compared with the distance between the pumping and leaking region. Pores which allow free passage of ions will therefore provide a region of negligible electrical resistance across the membrane. It is a similar situation which generates the action potential in nerve fibres. With *Chara* cells of membrane potential 140 mV, a cytoplasmic viscosity of 60 centipoises, and a ζ-potential of 40 mV, the spacing between the pores should not be greater than 0·5 μ to produce a rate of streaming of 60 μ per sec. Our knowledge of membrane structure suggests that the interpore distance is likely to be less than this; the values of the resistances in the cells that would establish this ζ-potential have not yet been measured, but experiments are currently in progress in these laboratories to measure them. The force produced by electro-osmosis should therefore clearly be adequate to drive the cytoplasm. Provided that the leaks and pores, or the charge density, are unsymmetrically arranged,

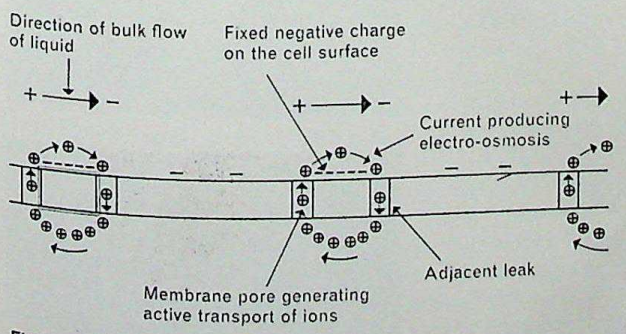

Direction of bulk flow of liquid
Fixed negative charge on the cell surface
Current producing electro-osmosis
Adjacent leak
Membrane pore generating active transport of ions

Figure 7 Electro-osmosis generated at the surface of a membrane by circular currents due to membrane pores.

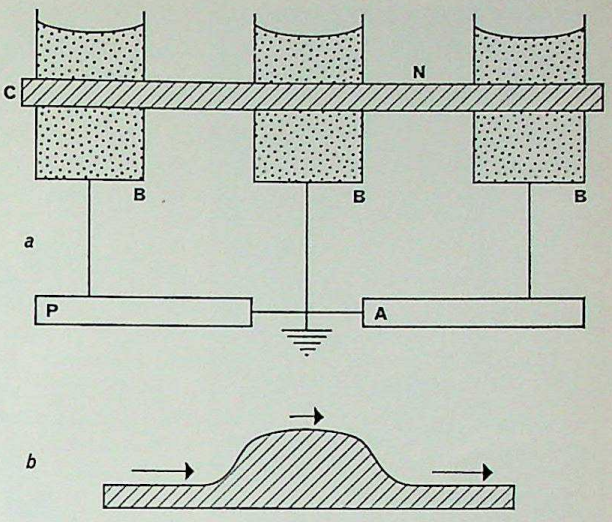


Figure 8 (*a*), Arrangement of *Nitella* cell for studying action potentials; *B*, saline baths separated by insulating layer of vaseline; *P*, pulse generator; *N*, *Nitella* cell; *A*, d.c. amplifier; (*b*), accumulation of cytoplasm in region of cell stimulated by electrical pulse. Arrows indicate streaming velocity.

and this, again, has to be tested experimentally, the system will drive the water round the cell in a circular path. It should be possible to test the correctness of the model by electrical and magnetic field experiments with living cells.

The existence of the local circular currents shown in figure 7 can be demonstrated during the passage of the action potential along nerve fibres. This travels rapidly along the fibre, at about 2 metres per sec in unmyelinated mammalian nerve, and in the region of the action potential the membrane potential changes from negative to positive. In order to generate electro-osmosis in plant cells, it must move very slowly or remain stationary. Particularly interesting in this respect are the investigations of the Japanese botanists U. Kishimoto and H. Akabori, who mounted *Nitella* cells in separated salt baths (figure 8a) [3]. By applying a pulse of 500 mV for 0·25 sec between *A* and *B*, an action potential was generated between *B* and *C*. The plant cell therefore generates an action potential similar to that developed by a nerve cell when an external potential is applied to reach the limit of membrane breakdown. These observations confirm those made by Harmer in 1898 and by Ewart in 1902. The action potential moves very slowly in comparison with its speed in nerve fibre, taking up to 30 sec to cover the distance as compared with about 1 msec for nerve. During this period protoplasmic streaming ceases. In other words, the maintenance of a steady membrane potential is necessary for protoplasmic flow. If the electrical mechanism involves the pumping of ions, as shown in figure 7, the addition of ions to the external medium should affect the streaming. This has been found to be the case by Kishimoto and Akabori and by Ambrose and Goldacre. Again, if the external potential is applied as shown in figure 8a, it will be added to the potential along the membrane in one case and will subtract from it when applied in the reverse sense. Kishimoto and Akabori found for example that stimulation by an anode was more effective than stimulation by a cathode. Ambrose and Goldacre examined streaming

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

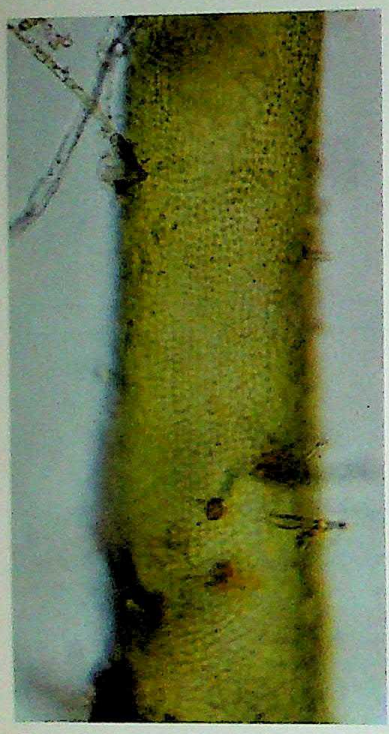


Figure 9 Apical cell of an alga (*Chara*).

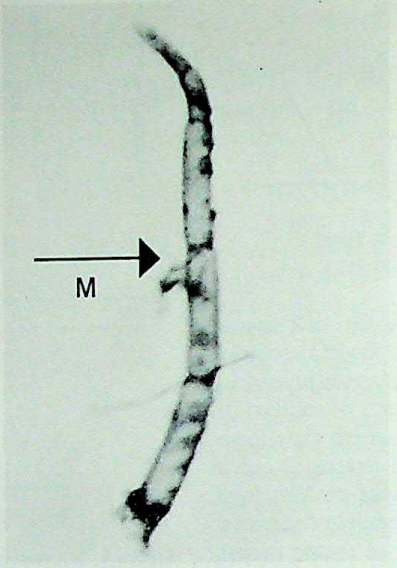


Figure 10 Actively streaming cell of *Chara* suspended in a hanging drop in a magnetic field. *M*, direction of magnetic field.

Figure 11 (right) Time lapse film of moving fibroblast, showing ruffles on the surface. The ruffles are seen to move with time.

in *Tradescantia* staminal hairs, where two strands streaming in opposite directions can be observed simultaneously. A critical pulsed potential can again be applied, and this arrests streaming in direction *A* before streaming stops in direction *B* (figure 12). Cytoplasm accumulates for a short time as shown. Here again stimulation by the anode is the more effective. Similar accumulation was observed by Kishimoto and Akabori in regions of stimulation in *Nitella* (figure 8b). These experiments favour the view that potential differences parallel to the membrane are involved in streaming.

The effects of magnetism

Perhaps the most convincing experiments are those using magnetic fields. This subject has interested physicists ever since the discovery of the electric current. The possibility that electric currents might be present in living cells was suggested by Amici in 1818, and Becquerel and Faraday realized that it should be possible to produce effects with magnetic fields. A number of workers have examined the effect of magnetic fields on streaming in algae, but with negative results. The subject was dropped for many years until taken up again by P. W. Ssawostin in 1924. After working for six years, first in Tomsk, later in Odessa and finally in Leipzig, he published an account [5] showing that magnetic fields did affect streaming. He worked mainly with *Vallisneria spiralis* and with *Elodea canadiensis*, and, unlike previous workers, he made accurate measurements of the velocity of streaming. He also had high field-strengths (7000 gauss) available, and the cells he used were more sensitive than were the algae that were previously used. He found that the velocity of streaming could be changed by as much as 40 per cent; in some cases it was increased, in others decreased, depending on the orientation of the cell. The author of this article has been able to confirm a number of Ssawostin's observations.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

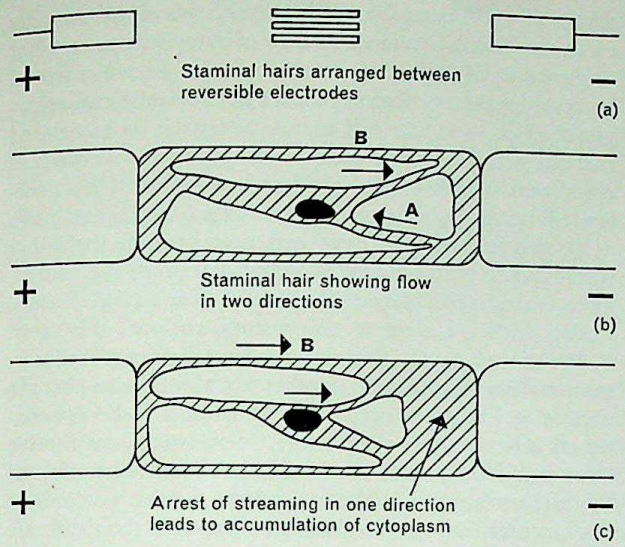


Figure 12 Effects of external electric field on streaming in *Tradescantia* staminal hairs. *a*, staminal hairs arranged between two reversible electrodes; *b*, streaming in two directions, *A* and *B*; *c*, arrest of streaming in direction *A*.

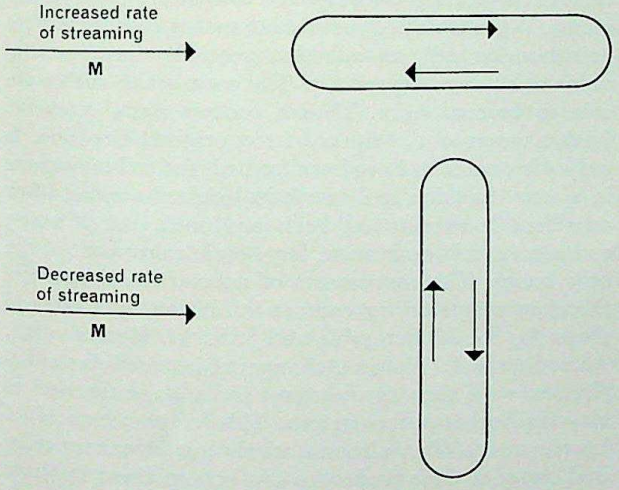


Figure 13 Effect of external magnetic field of 20 000 gauss on the rate of streaming in *Chara* cell. *M*, direction of external field.

One reason why the investigations at the turn of the century did not obtain positive results was that *Chara* is particularly insensitive to magnetic fields, but by using field strengths of 20 000 gauss, the author has obtained, even in this organism, changes in the velocity of streaming that depend on orientation (figure 13). The effect can also be demonstrated in *Plasmodia*.

The laws of electromagnetism show that circular currents such as those in figure 7 will produce a magnetic field at right angles to the plane of the current. Since the flow of water round a plant cell is circular, the local currents should produce magnetic fields that add together, and external magnetic fields will affect the circular currents of the cell to an extent that depends upon the orientation of the cell. However the cell is displaced by rotation of the tube in which it is enclosed, the cell quickly returns to its equilibrium position at right angles to the field. Ssawostin suggested that circular electric currents were involved, although at that time insufficient was known about cell membranes for any definite suggestion to be made as to mechanisms.

The clearest demonstration that cells generate magnetic fields is to show that they will behave like small magnets when suspended in a magnetic field. Figure 10 shows an apical cell of *Chara* suspended in a homogeneous magnetic field in a hanging drop of water free from surface film. The cell arranges itself at right angles to the magnetic field. If the cell is now removed from the drop and heated until protoplasmic streaming ceases, it lies parallel to the magnetic field. Now when a *Chara* cell is placed near an isolated pole, it moves towards the pole—the material in water is paramagnetic. It would therefore be expected to lie parallel to the lines of force in a homogeneous field, as does a piece of soft iron, although the forces operating are many thousands of times smaller. The orientation of the actively streaming cell at right angles to the field can only be explained in terms of a magnetic field generated by the living cell in opposition to its paramagnetism. These observations provide definite evidence that plant cells that show rapid cytoplasmic streaming in circular paths have an associated circular electric current.

The locomotion of whole cells

Animal cells move actively, and certain primitive plants are also capable of movement. Most of the pioneering work in this field was carried out on amoebae, particularly the large amoeba *A. proteus*, and active research still goes on in this field. However, the movements of amoebae are extremely complicated: many changes—pseudopod formation, large-scale streaming of cytoplasm, and sol-gel transformations—take place simultaneously. The author has therefore preferred to work with mammalian tissue cells in culture, where the movements are less complex and the region adjacent to the cell membrane appears to be mainly involved, as in plant cells. Figure 11 shows a series of pictures taken from a time-lapse film of a moving fibroblast in a culture medium. Ruffles or waves on the membrane can be seen on the leading edge of the cell. These ruffles form continuously on the leading edge of the cell and travel backwards towards the nucleus. In appearance, they are rather like the waves of the sea. The pictures shown in the plate were taken with an interference microscope, which shows changes of cell thickness as changes of colour in the image. It is also possible to examine the actual contacts between the cell membrane and the glass by means of a surface contact microscope. This microscope makes use of light totally internally reflected at a prism surface so that points of contact between the cell and the glass are seen as illuminated areas. It can be seen that these ruffling

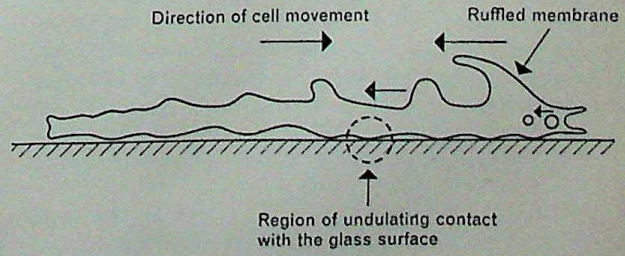


Figure 14 Cross section through a fibroblast moving on a glass surface.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

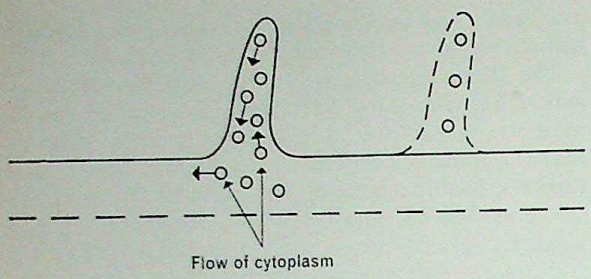


Figure 15 Cross section through a single ruffle on the membrane surface, showing how the cytoplasm may flow beneath the surface.

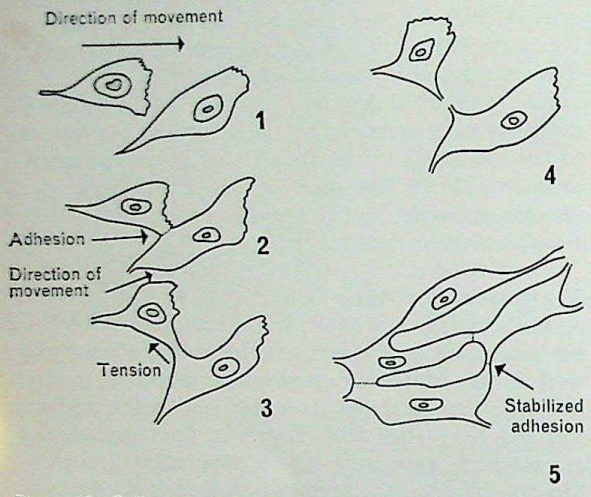


Figure 16 Cell contacts between normal fibroblasts. 1, moving fibroblasts; 2, formation of a contact; 3, stretching of a stable contact; 4, breaking of contact; 5, stabilized sheet of cells.

movements of the membrane are occurring over the whole area in contact with the glass (figure 15). The cell moves across the glass by making intermittent contacts generated by these peristaltic movements of the cell membrane. Here again the most obvious explanation is that given by Kamiya for cyclosis in plant cells and by Goldacre for amoeboid movement. Contractile proteins may be responsible, but a closer examination of the moving fibroblast shows that this explanation is not very satisfactory. A measurement of the amplitude of the ruffles on the leading edge of a roving fibroblast by interference microscopy shows that they may reach a height of five microns. This is three or four times the thickness of the remainder of the cell. In other words, these ruffles are waves of large-scale expansion that travel along the cell, and they must be generated by a force producing expansion within the cell. The generation of waves of cytoplasm by analogy with wave movements on the sea involves a circular flow of cytoplasm somewhat as shown in figure 14. Here again the implication would be that the motive force operates between the cell endoplasm or sol and the cell membrane with its associated cortical gel. To check this possibility, the movement of cytoplasm within these cells has been studied by time-lapse filming. It becomes apparent that cytoplasm flows at its maximum rate near cell membranes, including intracellular membranes. It looks as though the motive force is similar to that of cyclosis in plant cells. Recent studies with the electron microscope support this view. P. Weiss and A. C. Taylor have found microtubules in mammalian fibroblasts similar to those seen in the cortical gel of plant cells, and these tend to be concentrated near the cell membrane. Here again the motive force could be due to a reaction between the region of the microtubules and the endoplasm, which could lead to a circular flow of cytoplasm and hence to the rhythmic movements of the membrane ruffles.

The movement of mammalian cells is of importance in a number of aspects of the behaviour of the whole organism. Contacts with fibres control movement parallel to the orientation of these structures, and contacts between neighbouring cells also affect their movements. When a ruffled membrane makes contact with a neighbouring cell, an adhesion generally forms at the point of contact (figure 16). The membrane ruffles are seen to be stationary. Thus a contact signal prevents further movement of the cell in its original direction. If only a few contacts have been formed, the cell may move in a new direction and break its original contact after considerable tension has been produced. But if many contacts have been formed, large-scale movement of the cells ceases. The movements of normal fibroblasts are therefore regulated by contact inhibition, as has been shown by M. Abercrombie and J. R. M. Heasman [6]. According to L. Wolpert, changes of intercellular adhesiveness with time can account for a large fraction of all morphogenetic movements. This 'contact control' of movements is often almost entirely lost in cancer cells, and many of their properties can be explained in terms of this loss of contact regulation of growth and movement.

References

[1] Jarosch, R. *Phyton*, 6, 87, 1956.
[2] Kamiya, N. *Ann. Rep. Sci. Wks. Fac. Sci. Osaka Univ.*, 1, 53, 1953.
[3] Kishimoto, U. and Akabori, H. *J. gen. Physiol.*, 42, 1167, 1959.
[4] Ambrose, E. J. and Goldacre, R. J. (In press.)
[5] Ssawostin, P. W. *Planta*, 11, 683, 1930.
[6] Abercrombie, M. and Heasman, J. R. M. *Expl Cell Res.*, 5, 111, 1953.
[7] Weiss, P. and Taylor, A. C. IOPAB International Biophysics Meeting, Abstract B IV. 5. Paris, 1964.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

The Xanthidia

Digitized by Arya Samaj Foundation Chennai and eGangotri

William A. S. Sarjeant

Many of the difficulties of using fossils to date geological strata are avoided by using microfossils with shell walls composed of organic compounds. These are abundant, widespread, and resistant to metamorphic changes. One group—originally called Xanthidia—was discovered in 1836 but was of little value until recently, because its origins were so little understood. Now that these have been determined, the group is proving extremely valuable to geologists both in commercial studies and in such archaeological work as demonstrating the source of stone-age axes.

Fossils are of prime importance to the geologist, not just for their own sake as interesting objects and as vestiges of past life on Earth, but also as the principal key for the determination of the succession of the rocks. Successive sedimentary rock units contain different assemblages of fossils, and these differences result from the combined effects of evolution and changing conditions. The palaeontologist, from study of a group of fossils, can thus determine both the relative and the absolute age of the sediment in which they were found. If the succession of fossil assemblages, and hence of strata, at a number of different points is known, the structure of the rocks and position of any folds or faults can be determined. This information is of prime importance to the miner tracing his lode or seam, the petroleum engineer seeking oil-bearing structures, and the civil engineer choosing sites.

The task of the palaeontologist is, however, complicated by a number of factors. The distribution of animals and plants at the present day is closely controlled by environment; this control obviously applied with equal force in the past. Some sediments, such as those from the Triassic deserts, are almost barren of fossils. All groups of organisms do not evolve at the same rate—some change rapidly, others scarcely at all over millions of years. For example, many beds in the Upper Carboniferous of England contain only Lingulids, a group of brachiopods that survived too long to be useful for accurate dating. Again, sediments accumulating in shallow water are likely to contain a suite of fossils entirely different from that in sediment forming at the same time in deeper waters or on land. In each suite, some group of fossils may have been present that was evolving rapidly enough to make it possible to establish a sequence of zones, each characterized by particular forms, but precise correlation of the shallow-water zones with the deeper-water or the terrestrial zones may be very difficult. An example is the difficulty of correlating the non-marine Purbeck and Wealden beds of southern England with their marine equivalents on the Continent of Europe.

Another problem is that an adequate number of fossils is needed. Only rarely is a single fossil determinative; the use of only a few fossils can give misleading results. Further, the sediment itself may be altered by heating or stress, or both, under the effects of earth movements. The resultant reorientation of particles, and chemical changes within the rocks, may partially or entirely destroy the fossils. Finally, ground-water circulation through permeable rocks may dissolve calcareous fossils, such as mollusc shells or foraminifera.

W. A. S. Sarjeant, *B.Sc., Ph.D., F.G.S.*,
Was born in 1935 in Sheffield, England, and educated at the University there. He subsequently went to University College of North Staffordshire, now Keele, and Reading University before taking up his present appointment as Lecturer in Geology at Nottingham University. His principal research interest is in the fossil microplankton and its use in stratigraphy. A second interest is in the mineralogy of Derbyshire.

Microfossils

Over the last decade, it has come to be realized that many of these problems may be solved by using groups of microfossils recognizable only at high magnifications (500–1500 diameters). These groups possess shell walls composed of organic compounds; they are extracted from sediments by a standard chemical technique described later. Their study is now called palynology.

The most familiar of the fossil groups studied by the palynologist are pollen and spores. These are present in great numbers in most sediments—concentrations of several hundred thousands of particles per gram are in no way unusual. Determinative assemblages thus can be extracted from quite small samples, which is important in the study of borehole cores. As the pollen and spores are distributed by wind and water, the same types may be present in both terrestrial and marine sediments. Finally, they are not subject to decalcification and will tolerate a quite considerable intensity of heat and stress before being destroyed [1].

However, there are some limitations. The present-day distribution of plants is closely controlled by climate. Vegetational zones are often quite narrow, generally parallel to the equator, but readily modified by, for example, changes in altitude. Fossil pollen and spores characterize similarly narrow vegetational zones; correlations over long distances are therefore difficult. Another limitation is that the concentration and variety of spores and pollen in sediments change sharply offshore, and relatively deep-water sediments contain only saccate pollens, restricted in variety and composed of types that were unchanged for long periods of time.

The attention of palynologists has therefore increasingly focused on other groups. For example, the Chitinozoa, a group of flask-shaped organisms present only in Palaeozoic marine sediments, have been used successfully as stratigraphic indexes by French oil companies operating in the Sahara [2, 3]. However, I should like to consider some groups of fossils that are present in great number and variety in marine sediments throughout the geological column. These groups have long been known to geologists, but they have only recently been sufficiently understood to be used in solving geological problems.

Dinoflagellates

In 1836 a great German microscopist, Christian Gottfried Ehrenberg, astonished the scientific world by demonstrating to the Berlin Academy that large masses of rock,

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

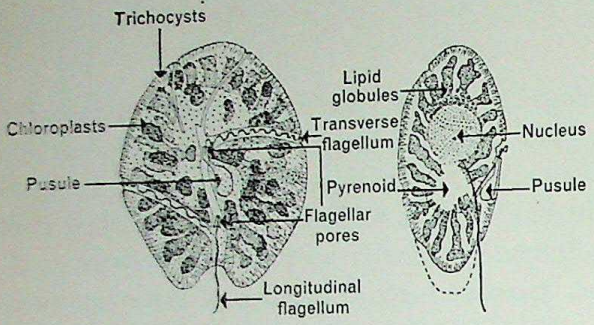


Figure 1 A typical modern unarmoured dinoflagellate, *Gyrodinium pavillardi*, in ventral (left) and lateral views. (Redrawn after B. Biecheler.)

whole strata, were made up entirely of the remains of microscopic animals and plants. He showed that the polishing earth called tripoli was just an accumulation of siliceous shells of Diatoms or Radiolaria, and that chalk was composed of untold millions of Coccoliths, tiny calcareous plates of algae.

Among the flood of new forms he described were two groups encountered in thin flakes of Jurassic and Cretaceous cherts and flint. One group comprised minute (10–200 μ) spherical to polygonal shells, semi-transparent, and having a characteristic median furrow. These Ehrenberg immediately recognized: they were dinoflagellates, a group he had often studied in living plankton.

They are a group of great ecological importance, since they occur in enormous abundance in plankton and rank second only to the diatoms as a primary source of food in the sea. Their basic structure is a simple cell surrounded by a softer outer pellicle that carries two flagella (figure 1). Some, however, possess an enclosing 'armour' made up of a more rigid organic substance and sub-divided by ridges into a pattern of plates (figure 2): the micro-fossils found by Ehrenberg showed such a subdivision. The dinoflagellates are a group straddling the boundary between the animal and plant kingdoms—some contain chloroplasts and feed holophytically, by photosynthesis; some are saprophytic, feeding off other micro-organisms; some have a mixed diet; and some start life with chloroplasts and later lose them, becoming secondarily saprophytic. Their classification is accordingly difficult; to the zoologist they are animals and are classed in the Order Dinoflagellata, but to the botanist they are plants and to be placed in the Order Dinophyceae. Most biologists would nowadays treat them as algae and hence plants, since the presence of chloroplasts is considered a more decisive evidence of plant affinity than is a saprophytic habit of animal affinity.

Xanthidia

A second group of fossils, discovered by Ehrenberg in his chert and flint flakes, presented more of a problem. These were small spiny bodies, similar in size and general appearance to his dinoflagellates. Some of them showed a surface division into plates and even a median band corresponding to the transverse furrow; but it was straddled by spines and could never have contained a flagellum. Others lacked any such divisions; they were simply spheres bearing thorn-like or tubular processes, distributed in apparently quite random fashion over the whole surface. Ehrenberg was reminded of a freshwater desmid which he had discovered and named *Xanthidium*, and he put them into this genus. He considered that they and the dinoflagellates consisted of silica—either the original shell was siliceous, or else it had been secondarily silicified; he does not seem to have found it surprising that *Xanthidium*, which he knew to be a freshwater organism, should occur in marine deposits.

The systematic allocation of the spiny spheres was to prove a cause of considerable controversy, begun by a French microscopist, C. R. Turpin. His criticism was published in 1837 [4], actually one year before Ehrenberg's original findings were published [5]. Turpin accepted that the shells were silicified, but considered them to be the mobile young stages, or statoblasts, of the Bryozoon *Cristatella*, a sessile colonial organism of fresh water.

British interest in the group was stimulated by a visit to London by Ehrenberg in 1838: a number of members of the Clapham Microscopical Society described these fossils and, like Ehrenberg, called them '*Xanthidia*'. The Society's most eminent member, the great palaeontologist G. A. Mantell, was, however, more critical. Careful

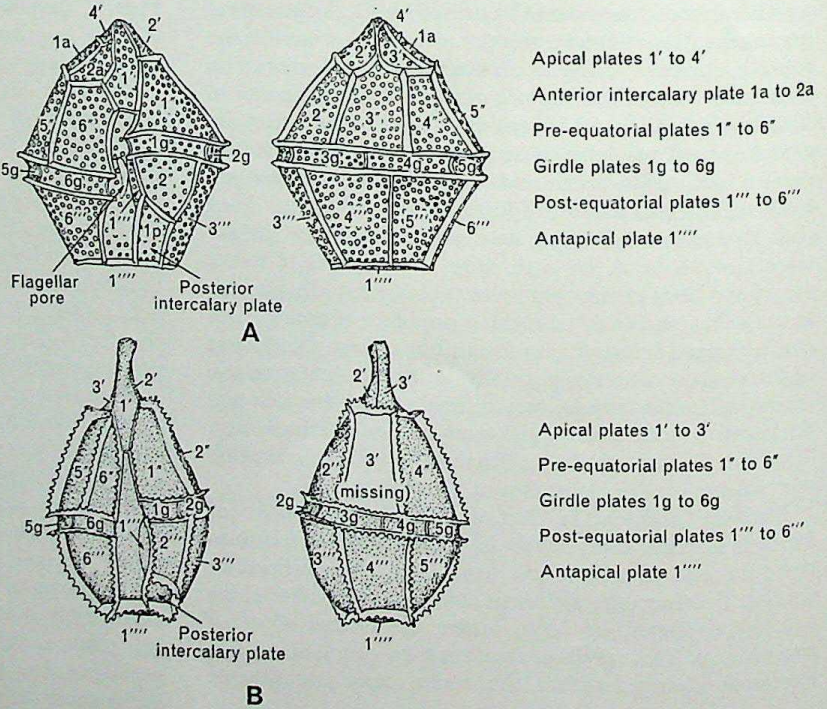


Figure 2 The tabulation of a modern dinoflagellate compared with that of a fossil dinoflagellate cyst. A. *Gonyaulax polyedra*, a dinoflagellate of present-day warm and temperate seas. (Redrawn from Kofoid.) B. *Gonyaulacysta jurassica*, a dinoflagellate cyst from the Jurassic, with an archaeopyle formed by loss of a single pre-equatorial plate.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

examination showed him that the microfossils were regularly deformed or shrivelled, a characteristic that did not fit with the concept of siliceous shell; in addition, they charred when heated, which conclusively indicated an organic composition. They were therefore not *Xanthidia*. Mantell proposed instead the name *Spiniferites* —unfortunately in a footnote, so that the suggestion came to be entirely overlooked [6, 7]. He suggested that these organisms might be 'gemmules of polyparia or the spores of marine plants'.

Mantell's observations were sound, but they attracted little notice. In describing an assemblage from Texas, the American J. A. Merrill repeated Ehrenberg's error of supposing them to be siliceous and suggested that they were spicules (skeletal elements) of sponges [8]. The year 1905 saw the publication of two contrary opinions by German palaeontologists. Theodor Fuchs suggested that they were egg-cases of copepods, a group of planktonic crustacea [9]. P. F. Reinsch, on the other hand, considered them to be cysts—non-living membranes enclosing cells—of the type of those secreted by dinoflagellates during reproductive or resting stages, and suggested the name 'palinospheres' [10]; but this name has never come into general use. The term '*Xanthidia*' continued in intermittent use until as late as 1932 [11].

In 1933, however, a monumental study of Upper Cretaceous microplankton, again based on examination of flint chippings, was made by another German, Otto Wetzel [12]. Wetzel rejected the attribution to *Xanthidium* and instead placed the spiny spheres in his new genus *Hystrichosphaera:* he was unable to come to any conclusions regarding their affinity. Subsequent research brought discovery of additional genera; the group was expanded into an order, Hystrichosphaeridia, of uncertain systematic position, and the group came to be known familiarly as the hystrichospheres.

This uncertainty regarding their affinity was a serious handicap, and not merely because any question mark in science is a constant irritant. Firstly, they could not be classified. Were they animals or plants? Until this was established they could be described under two separate nomenclatural codes which, although broadly similar, differ considerably in detail. Were they independent mature organisms, or were they merely plant spores or crustacean eggs? The botanical code contains provision for natural Linnaean genera, and also for the use of distinct names for separate parts of plants or for stages in their life cycle and for the naming of organisms on the basis of shape alone, without further biological implication. The zoological code is much more rigid and permits only natural genera: the crustacean egg must have the same name as the adult—an excellent state of affairs for the biologist who knows the life history, but much less satisfactory for the palaeontologist, who might never prove any link, or who, having proved it, might be faced with abandoning a well-established and convenient name. The result was a confused situation which was likely to worsen. Secondly, until the nature of the organisms was known, they could provide little information regarding the environment in which the sediments were formed. The hystrichospheres were found only in marine sediments; did this mean they lived only in saline conditions? If so, this would be of profound interest. The geologist is frequently confronted by beds which could have been formed equally well in a shallow sea, in an estuary, or even under freshwater conditions; a fossil that was a consistent index of marine conditions would be extremely useful.

Recent studies

In 1947, the great French microscopist, Georges Deflandre, who has made a number of pioneer studies in this field, reviewed available information on fossil forms and on analogous living plankton [13]. He concluded that the hystrichospheres were certainly marine organisms and, from their wide distribution in different lithologies, most probably plankton. However, he felt that they were not a single group, but contained representatives of a number of different groups—algae, cysts of algae, eggs of higher organisms, perhaps even some spores. These views were echoed by the present author in a review [14].

The main advocate of the contrary view was, and is, the German palaeontologist, Alfred Eisenack, who was the first to undertake research on Palaeozoic assemblages. Eisenack believes emphatically that the spiny cysts form a single taxonomic unit [15]. He points out that their morphology, although variable, varies within relatively narrow limits; the basic form is a hollow sphere with or without radiating outgrowths, and from this all known morphological types can be derived. The shells frequently show openings, all more or less of the same kind. The wall substance appears to be of constant composition. Its precise nature is unknown—it is not cellulose, protein, chitin, or tectin, all these being determinable substances characteristic of particular groups of organisms. It appears instead to be a macromolecular substance resembling cutin or sporopolennin. From these evidences Eisenack considers these organisms to be an order of unicellular algae, planktonic or benthonic.

However, recent detailed studies of the morphology of fossil dinoflagellates and hystrichospheres, started by the American palaeontologist W. R. Evitt, have gone far towards exploding this view [16, 17]. Evitt pointed out that the shells of fossil dinoflagellates frequently showed an opening of some kind, formed either by the loss of a single plate or a group of plates, or by schism of the shell into two halves along, or parallel to, the line of the transverse furrow. Such an opening is termed an archaeopyle. It is clearly an exit, through which the organism left the shell after a resting period or after fission (figures 2, 11, and 12).

Now, study of fossil assemblages shows that openings are present in the shells of hystrichospheres. Sometimes they are circular, which proves nothing. In other cases, however, they are polygonal, with a shape and situation paralleling the archaeopyles of dinoflagellates. There is no conceivable reason why an opening in a spherical or ovoidal shell should be polygonal unless the shell had polygonal elements—such as the plates of dinoflagellates —in its structure.

Certain hystrichospheres show a transverse band of some kind, analogous to the transverse furrow of dinoflagellates; some show also a surface differentiation into fields corresponding to the fields of a dinoflagellate. The type species, *H. furcata*, of *Hystrichosphaera* and thus of the entire group, possesses both these features. The presence of spines arising from the transverse band caused Otto Wetzel rightly to conclude that the band could not have contained a flagellum. However, if *Hystrichosphaera* is visualized, not as a motile dinoflagellate but

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

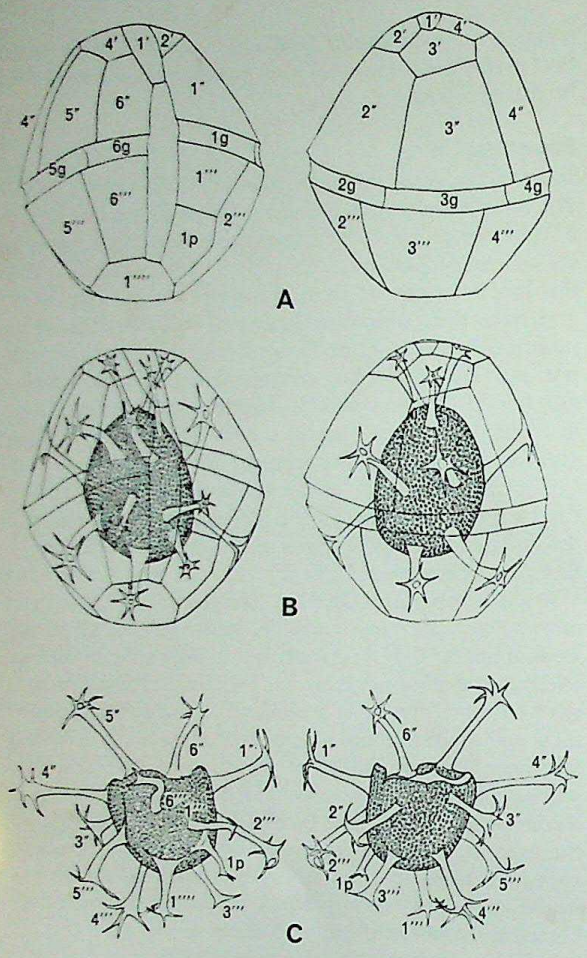


Figure 3 Reconstruction of the original tabulation of a dinoflagellate from the distribution of processes in a cyst of 'hystrichosphere' type. A. The probable original tabulation of the dinoflagellate, which accords with that of *Gonyaulax*. (The apical tabulation is entirely hypothetical.) B. The cyst forming within the dinoflagellate, attached to the outer wall by its processes. C. The abandoned cyst, with an apical archaeopyle, after crushing and distortion resulting from consolidation and compaction of the sediment (*Hystrichosphaeridium vasiformum*, a species from the Lower Cretaceous Speeton Clay of England).

simply as a cyst, this ceases to be a problem and its dinoflagellate character becomes obvious.

Evitt carried his studies a stage further. By careful study of large numbers of individuals of the same few species, for example in the genus *Hystrichosphaeridium*, he found that the numbers of spines were constant. In addition the spines showed a constant positional relationship and even a constant variation in relative size. Their positions correspond to these of the plates of a dinoflagellate; their relative size corresponds to the proportional size of the particular plate they represent. From this he deduced that some, at least, of the hystrichospheres were cysts formed within the cell wall of the dinoflagellate and initially linked to it by processes (figure 3). Recent studies by Martine Rossignol and by Evitt of material in present-day sediments from the coasts of Israel and California have produced examples of all stages between the original dinoflagellate and the final abandoned cysts [18, 19].

A corollary to all this is that the fossils already recognized as dinoflagellates are themselves also cysts, since they, too, are breached by archaeopyles. They differ from the hystrichospheres, of the type of *Hystrichosphaeridium* and *Hystrichosphaera*, only in their higher degree of resemblance to the outer wall of the motile stage. This may merely mean that the cyst formed nearer the cell wall.

When those hystrichospheres showing features of affinity to the dinoflagellates have been reattributed to that group, a number of genera remain, in which the shells are either unperforated or perforated by a simple circular opening, and in which the processes show a quite random distribution. Some of these are spherical to oval forms, with a thick wall perforated by a system of pores; these forms have been shown by D. Wall to be attributable to another group of algae, the chlorophyceae, and comparable to such modern genera as *Pachytheca* [20]. Even when those genera have been transferred, a large residue of forms of unknown systematic position remain. These can no longer be termed hystrichospheres, since the typical hystrichospheres, such as *Hystrichosphaera* itself, are demonstrably dinoflagellate cysts. The remaining forms are now classed into the group Acritarcha, a morphological grouping used for forms of similar general appearance and undetermined or intermediate affinity [21]. It is interesting to note that true hystrichospheres, like the undoubted dinoflagellates of pre-Evitt days, appear only in the Permian; the acritarchs, on the other hand, range right through from Pre-Cambrian to the present day.

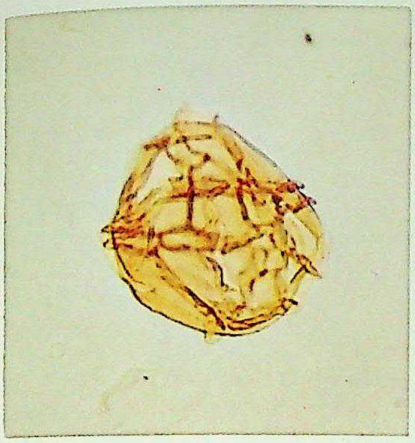
Modern records of hystrichospheres and acritarchs were, until recently, relatively few. They were recorded in 1875 by W. B. Carpenter [22], and occasional forms have been figured in the accounts of plankton expeditions, either as planktonic eggs or as forms of unspecified character—many of these records were gathered together by G. Deflandre in his 1947 review [13]. However, such records are few, possibly because the cysts are generally smaller than the finest mesh of plankton nets, more probably because they would tend to sink, rather than remain in the plankton. It was not until 1950 that a Swedish palynologist, G. Erdtman, encountered undoubted hystrichospheres in modern sediments from a Swedish fjord [23]. Since then they have turned up quite widely in bottom samples—from the entire length of the North American coast from Greenland to the Gulf of Mexico [24], from the Mediterranean, from a Pacific coral atoll [25], from the Niger delta, and even from abyssal Atlantic sediments, confirming Carpenter's record [26]. Non-marine acritarchs have been recorded from peats of south-western Australia [27], but all records of hystrichospheres to date have been from marine sediments.

Applications

Geologically, the study of these groups is proving of first importance. The early period of palynology, in which these microfossils were studied in thin flakes of chert or flint, is past. Instead, a standard chemical treatment is used, and it is possible to process a small sample in as little as 30 hours. As a result of these advances, assemblages have been obtained from virtually all types of marine sediments—from limestones, sandstones, shales, clays, from petroleum, even from phosphates and salt.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri



4

5

6

7

8

9

Figure 4 Owing to the transparency of the shell, both surfaces can be studied from a single specimen at different planes of focus: here the ventral surface is seen obliquely in the upper plane, the dorsal surface being then seen by focusing lower. A typical dinoflagellate cyst, *Gonyaulacysta millioudi*, from the Upper Jurassic of Switzerland.

Figure 5 The shell is frequently almost colourless; a staining technique may be used to facilitate study. Safranin is the stain used here. An undescribed species of *Gonyaulacysta* from the Tertiary of Australia.

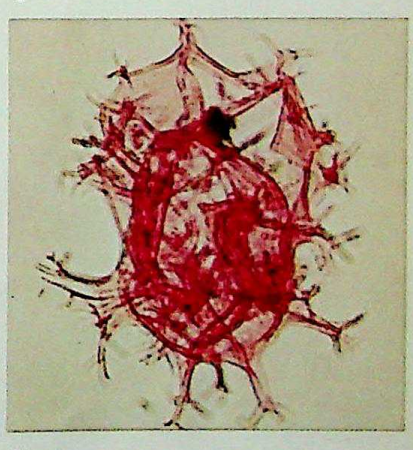
Figure 6 In order to see detail of the shell surface, phase contrast is frequently used. Specimen as last.

Figure 7 Dinoflagellate cysts – in particular those of the 'hystrichosphere' type, with long processes – frequently become enmeshed in organic debris, which may render their study much more difficult. *Hystrichosphaeridium cribrotubiferum*, from the Oxford Clay (Upper Jurassic) of England.

10

Figure 8 The earliest known British dinoflagellate cyst, *Gonyaulax rhaetica* from the Cotham beds (Upper Triassic).

Figure 9 A dinoflagellate cyst from much more modern British sediments – *Wetzeliella* cf. *symmetrica*, from a post-Pleistocene marine clay. (Stained with safranin.)



11

Figure 10 A 'hystrichosphere' with processes which ramify and are linked in complex fashion. *Cannosphaeropsis caulleryi*, from the Oxford Clay (Upper Jurassic) of England.

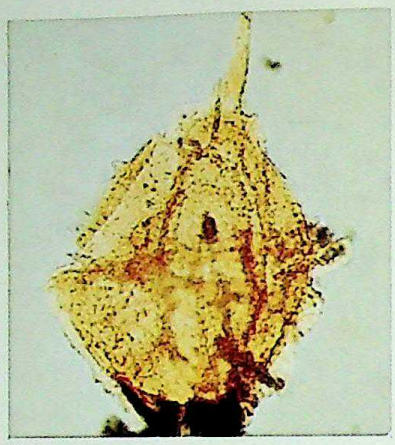
Figure 11 A specimen of the type 'hystrichosphere' from the Lower Chalk, *Hystrichosphaera furcata*, in which the encysted body appears to have not escaped from the cyst, despite the formation of the archaeopyle. (Stained with safranin.)

Figures 4–15 *Fossil Dinoflagellates.*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

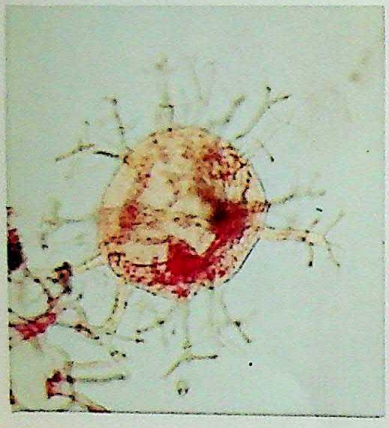
Digitized by Arya Samaj Foundation Chennai and eGangotri

12



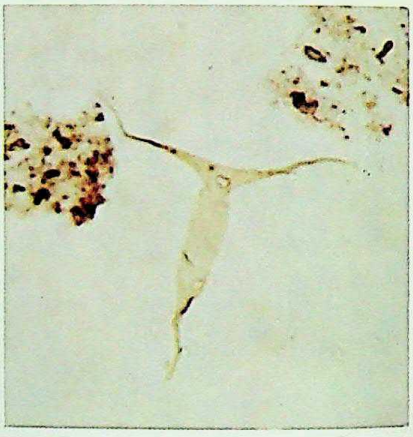
13

14



15

16



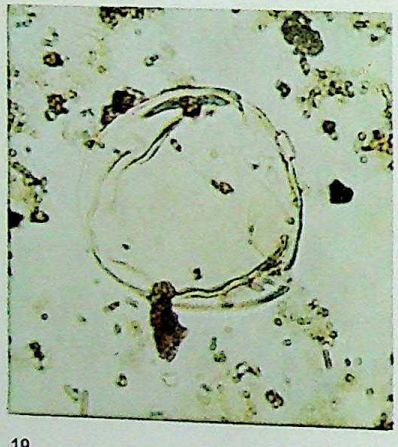
17

Figure 16 An acritarch with relatively few very long processes. *Baltisphaeridium longispinosum*, from the Hughley Shales (Silurian) of England.

18

Figure 12 A dinoflagellate cyst with a two-layered wall partially separated to form intramural cavities. *Scriniodinium campanula*, from the Lower Chalk (Upper Cretaceous) of England. (Stained with safranin.)

Figure 13 A large, heavily ornamented dinoflagellate cyst, unusually deeply coloured by humic substances. *Cribroperidinium sepimentum*, from the Speeton Clay (Lower Cretaceous) of England.



19

Figure 14 A dinoflagellate cyst with a dense reticulate ornament; without tabulation but with a distinct transverse furrow. *Scriniodinium dictyotum*, from the Sandsfoot Clay (Upper Jurassic) of England.

Figure 15 A dinoflagellate cyst of 'hystrichosphere' type, with branching spines. *Hystrichosphaera crassipellis*, from the Lower Chalk (Upper Cretaceous) of England.

Figure 17 A distinctively angular form, *Domasia* cf. *elongata*, also from the Hughley Shales.

Figure 18 An acritarch with many short processes, *Baltisphaeridium* cf. *hirsutoides*, from the Shineton Shales (Lower Ordovician) of England. The shell is packed with pyrite, as also is that in figure 16. This mineral greatly adds to the difficulty of study and cannot readily be removed by chemical treatment.

Figure 19 A simple spherical acritarch without processes, *Leiosphaeridia* cf. *similis*, from the Speeton Clay (Lower Cretaceous) of England. The shell shows a simple circular opening, a pylome, which affords no indication regarding affinity.

Figures 16–19 *Fossil Acritarchs*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Non-marine deposits have only rarely yielded assemblages, but dinoflagellates and acritarchs have been recorded from peats [27] and lignites [28].

In the period since 1933 dinoflagellates have been found very widely in Mesozoic and Cainozoic rocks. The earliest definite record at present is from the Permian [29], but a microfossil recently recorded from the Silurian of Tunisia, *Arpylorus*, has a polygonal lateral archeopyle and may well be a dinoflagellate [30]. Acritarchs are present throughout the geological column; forms with a very simple structure are known far back into the Pre-Cambrian, certainly from sediments older than 550 million years [31].

The numerical abundance is often extremely great: as many as 10 000 individuals may be present in a single gram of rock. Geographical distribution of particular species is often extremely wide; this is, of course, to be expected in planktonic organisms whose distribution is controlled, not by bottom conditions, but by the temperature and chemistry of the water body itself. Thus, for example, the author has seen the same species (*Gonyaulacysta longicornis*) from the same horizon in Britain, Germany, the Middle East, and Australia.

The rate of evolutionary change of these fossils is variable. In the Pre-Cambrian, the acritarchs are probably the only group of fossils to have been successfully used for establishing stratigraphic correlations, as for example between Scotland and Russia [32]. However, only broad correlations emerge, and the acritarchs of that age are of too simple a character to afford much prospect of more refined stratigraphic use. In the Lower Palaeozoic, acritarchs are present in great number and variety and are already widely in use as stratigraphic indices. The Upper Palaeozoic and Lower Mesozoic assemblages remain relatively little-known; such few extended studies as have been made suggest that the rate of evolution at this time was slow, making their potential stratigraphic value slight.

From the Middle Jurassic onwards, however, dinoflagellates are present in great number and variety; they can be used to establish a zonation as fine as that resulting from study of ammonites. Indeed, the combination of wide geographic and lithologic distribution, considerably vertical variability, and high concentration makes these groups ideal zonal fossils.

The composition of the shell means that, like spores, they are unaffected by decalcification and are capable of surviving quite a high degree of metamorphism [1]. Also, like spores, they are particularly useful in stratigraphic studies where only small samples are available, as in boreholes. In conglomerates, the pebbles would be expected to contain distinctly different assemblages from the matrix; thus both the source of the pebbles and the date of its accumulation may be determined. Studies of this type have been successfully carried out on Palaeozoic sediments in Bolivia [33]. Boulders carried to the sea by Antarctic glaciers have been shown, by means of their acritarch content, to be derived from Cambrian sediments buried under the ice [34]. Flint tools made by Protomagdalenian and Magdalenian man have been shown to be from particular sources in France by means of their dinoflagellate and acritarch content [35, 36].

Even today, the dinoflagellates and acritarchs remain comparatively little-known fossil groups. There was a hiatus of 80 years between the work of Ehrenberg and his followers in the 1850s and the recommencement of serious studies by Wetzel. Only in the last two decades has their commercial and geological significance come to be realized. With this realization has come an immense increase both in the number of specialists working on the group and in the volume of publications treating with them. Much more still remains to be learned regarding their stratigraphic distribution and affinities. Knowledge of the ecology of these organisms may have profound commercial repercussions, since the plants of the plankton are one of the ultimate sources of petroleum.

Acknowledgments

The assistance in photography of Mr J. Eyett of the University of Nottingham is gratefully acknowledged. The courteous loan of specimens for photography by Dr D. M. Churchill of the School of Botany, Cambridge (figures 2, 3, and 9); the Director of the Geological Survey of Great Britain (figure 8); Dr Charles Downie of the University of Sheffield (figure 7); and Messrs R. Batey and R. J. Davey of the University of Nottingham (figures 11, 12, and 15–18) is also acknowledged.

References

[1] Wilson, L. R. *Tulsa geol. Soc. Dig.*, 29, 131, 1961.
[2] Taugourdeau, P. and Jekhowsky, B. de. *Rev. Inst. franç. Pétrole*, 15, 1199, 1960.
[3] Kozlowski, R. *Acta palaeont. pol.*, 8, 425, 1963.
[4] Turpin, C. R. *C.R. Acad. Sci., Paris*, 4, 304; 351, 1837.
[5] Ehrenberg, C. G. *Abh. K. Akad. Wiss., Berlin*, 1, 109, 1838.
[6] Mantell, G. A. *Ann. Mag. nat. Hist.*, 16, 73, 1845.
[7] *Idem.* 'A pictorial atlas of fossil remains'. Bohn, London. 1850.
[8] Merrill, J. A. *Bull. Mus. comp. Zool. Harv.*, 28, 1, 1895.
[9] Fuchs, T. *Zbl. Miner. Geol. Paläont.*, 340, 1905.
[10] Reinsch, P. F. *Ibid.*, 402, 1905.
[11] Schuh, F. *Z. dtsch. geol. Ges.*, 84, 677, 1932.
[12] Wetzel, O. *Palaeontographica*, 77, 141; 78, 1, 1933.
[13] Deflandre, G. *Bull. Inst. océanogr. Monaco*, No. 918, 1, 1947.
[14] Sarjeant, W. A. S. *Grana Palynol.*, 2, 102, 1961.
[15] Eisenack, A. *Biol. Rev.*, 38, 107, 1963.
[16] Evitt, W. R. *Micropalaeontology*, 4, 385, 1961.
[17] *Idem. Proc. nat. Acad. Sci., Wash.*, 49, 158, 298, 1963.
[18] Rossignol, M. *Bull. Mus. Hist. nat., Paris*, 35, 207, 1963.
[19] Evitt, W. R. 'Dinoflagellate cysts and thecae'. (In press.)
[20] Wall, D. *Geol. Mag.*, 99, 353, 1962.
[21] Downie, C., Evitt, W. R., and Sarjeant, W. A. S. *Stanf. Univ. Publ. geol. Sci.*, 7, 1, 1963.
[22] Carpenter, W. B. 'The Microscope and its Applications'. Churchill, London. 1875.
[23] Erdtman, G. *Geol. Fören. Stockh. Förh.*, 72, 221, 1950.
[24] Wilson, L. R. and Hoffmeister, W. S. 'Morphology and Geology of Hystrichosphaerids'. Paper to Geological Society of America, 1954.
[25] McKee, E. D., Chronic, J., and Leopold, E. B. *Bull. Amer. Ass. Petrol. Geol.*, 43, 501, 1959.
[26] Williams, D. B. Personal communication.
[27] Churchill, D. M. and Sarjeant, W. A. S. *Grana Palynol.*, 3, 29, 1962.
[28] Traverse, A. *U.S. Dept. Interior, Bureau of Mines, Rep.*, No. 5151, 1, 1955.
[29] Tasch, P. *Micropalaeontology*, 9, 332, 1963.
[30] Calandra, F. *C.R. Acad. Sci., Paris*, 258, 4112, 1964.
[31] Roblot, M.-M. *Ibid.*, 256, 1557, 1963.
[32] Naumova, S. N. and Pavlovsky, E. V. *Dokl. Akad. Nauk SSSR*, 141, 181, 1961.
[33] Millioud, M. Personal communication.
[34] Vialov, O. S. and Timofeyev, B. V. *Dopov. Akad. Nauk URSR*, 10, 1134, 1959.
[35] Valensi, L. *Bull. Soc. préhist. fr.*, 52, 584, 1955.
[36] *Idem. Ibid.*, 57, 80, 1960.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Recombination of ions and electrons

Manfred A. Biondi

The recombination of ions and electrons is an important process in ionized media—even those on a geophysical and astrophysical scale—and thus has a pronounced influence on long-distance radio communication. In astrophysical cases the details of the process were ignored until recently, as it was assumed that it took place under conditions of thermodynamic equilibrium. The assumption is often not valid, and this article discusses theoretical and experimental methods of investigating the details of the collision reactions that are involved.

The term recombination is used to describe the processes whereby a positive ion interacts with an electron or a negative ion to form at least one neutral atom or molecule [1]. In electron-ion recombination, the free electron is captured by the positive ion; in ion-ion recombination the electron, in effect, transfers from the negative ion to the positive ion. Recombination processes play an important role in the neutralization of charge carriers in an ionized gas—a plasma—and, since the neutral atoms formed may be in electronically excited states, recombination is sometimes the source of a substantial portion of the optical radiation emitted by ionized media.

The recombination of ionized atoms with electrons or with negative ions is of importance in plasmas on both a small and a large physical scale. The light output in arc lamps is produced in part by recombination, and some striking geophysical effects—such as the emission of characteristic red and green lines in the nightglow from the Earth's upper atmosphere—are believed to result from a highly efficient recombination process occurring in these ionized layers. This same recombination process evidently limits the concentration of ions and electrons produced by the solar ultraviolet rays that strike the sunlit side of the atmosphere, and it affects the decay of this concentration on the night side of the Earth. As a result, recombination processes influence long-distance radio communications, which use signals bounced from the ionized layers of the upper atmosphere.

In astrophysics, there is a lively interest in the recombination processes that can take place in the outer layers of the Sun, such as the chromosphere and the corona. It had previously been assumed that the layers were in thermodynamic equilibrium, and the details of the ionization and recombination processes were ignored in calculating the radiation emitted from these layers. It has recently become apparent that the assumption of equilibrium is invalid in the tenuous corona, and even in the underlying chromosphere. Here, in a completely ionized medium, one must concern oneself with the effects of processes different from the usual two-body encounters between charged particles; new recombination mechanisms are involved.

Much of our information concerning recombination processes is derived from experimental studies carried out in the laboratory. The simplest method, in principle, for such studies is to form beams of the charged particles under study, to let them cross in an interaction region, and to observe the recombination that takes place in this region. In practice, it has not been possible to create charged-particle beams that are dense enough to yield a recombination signal stronger than the noise inherent in the measurements, although attempts have been made sporadically for several decades. The recombination measurements are therefore carried out in plasmas, and one is faced in the laboratory with difficulties of the same type as are encountered on a geophysical or astrophysical scale; in addition to recombination, many other processes of excitation, ionization, and particle transport occur in the ionized medium. Consequently, considerable patience and ingenuity are required to achieve conditions simple enough for the recombination to be determined unambiguously.

Manfred A. Biondi, *B.S., Ph.D.*

Was born in New Jersey in 1924 and educated at the Massachusetts Institute of Technology. He is now Professor of Physics at the University of Pittsburgh. His researches have been carried out in the fields of atomic collisions and plasma physics; and in superconductivity and the optical properties of metals at low temperatures.

Electron-ion recombination processes

In order to understand the mechanisms that lead to charged-particle recombination, let us first consider the energy states of the system of atomic particles involved. Figure 1 shows a schematic energy-level diagram for excitation of the outermost—optical—electron of an atom A. The normal or ground state of the atom is indicated by the symbol A, and the optical electron is indicated as being in a particular bound but excited state by the symbol A^*. It will be noted that the bound state energies converge to a limit above which the electron is free of the atom; that is, the atom is ionized. Above this level, the electron can take on any value of energy, and so a continuum of states, corresponding to the electron's having positive kinetic energy at infinity, results. The open circle indicates one possible state of the system $A^+ + e^-$. If the atom can capture an electron into a stable bound state, then the state A^- must lie below the state $A + e^-$. Since figure 1 lacks the additional electron to display this feature properly, the state A^- indicates the position of the bound state relative to the state $A + e^-$ in which the atom is in the ground state and the electron is at rest at infinity.

There is an approximation to thermodynamic equilibrium in some plasmas, so that the behaviour of the particles can be characterized by a temperature T. In this case there is no need to know the detailed recombination mechanisms to predict the concentrations of positive ions, electrons, and negative ions. It is necessary to know only the ionization potential of the atom, its electron affinity (binding energy for negative ion formation), and the statistical weights of the states involved. To illustrate, if we neglect negative ion formation for the moment, statistical-mechanical arguments lead to the

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

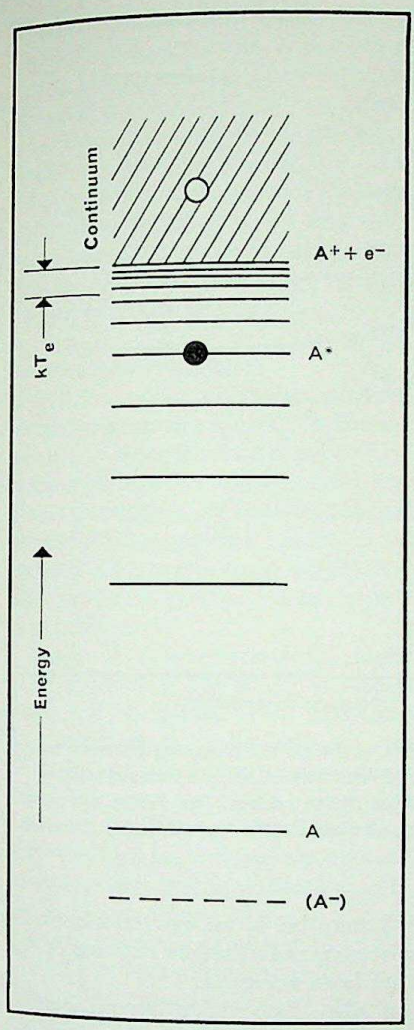


Figure 1 Schematic representation of the energy levels of an atom, A, indicating the positions of electronically excited states and the ionization continuum.

following form of Saha's equation relating the concentrations of positive ions (n_+), electrons (n_e), and normal atoms (n_n) present in a plasma at temperature T:

$$n_+ n_e / n_n = (2\pi m_e kT)^{3/2} h^{-3} \exp(-eV_i/kT), \quad \ldots (1)$$

where m_e is the electron mass, k is Boltzmann's constant and h is Planck's constant. In the absence of negative ions, the near electrical neutrality of a plasma permits us to set $n_+ \simeq n_e$, so that the fractional ionization n_+/n_n may be calculated at any concentration and temperature of neutral atoms.

In most cases, the particles in the ionized medium are not approximately in thermodynamic equilibrium, and it is necessary to inquire into the details of possible recombination mechanisms [1]. Although there are various recombination processes that are quite different in character, we seek in each a means of binding the electron to the positive ion while providing a mechanism to take up the energy that is released as this occurs. We wish to take the electron from a state of positive energy (figure 1)—for example, the continuum state indicated by the open circle—and cause it to occupy a bound state of the atom (solid circle),

$$A^+ + e^- \rightarrow A^* + \text{energy} \quad \ldots (2)$$

An obvious mechanism for the release of this energy is the radiation of electromagnetic energy by the electron as it is accelerated in the field of the ion; in quantum mechanical terms, we speak of a radiative transition from a free to a bound state of the system. The energy released appears as a photon of energy $h\nu$, where ν is the frequency of the radiation. The rate of this radiative recombination can be calculated quite accurately by the use of quantum mechanics [1], provided that the wave functions for the atom in question are reasonably well known.

Radiative recombination is not a particularly effective means of electron capture; for example, for electrons having kinetic energies corresponding to room temperature ($\sim 300°K$), the capture cross-section Q_{rad} is less than 10^{-18} cm^2, and decreases with increasing electron energy. Ordinary collision cross-sections for atoms are of the order of 10^{-16} cm^2; thus, the small value of Q_{rad} indicates that the process has a low probability of occurrence at a single encounter between an electron and an ion.

There is the problem of disposing of the energy released in the recombination reaction, and one possibility is that some third body can provide the means of taking up the energy. If the concentration of charged particles or neutral atoms is sufficiently large, then there is a reasonable probability of finding a third body in the vicinity of the electron and ion while they are interacting strongly. For example, consider a plasma containing a moderate concentration of positive ions and electrons. As a result of the long-range Coulomb interaction among these particles, two electrons in the continuum (figure 1) can transfer energy while in the vicinity of an ion. This can lead to the capture of one electron into a bound state of the resulting atom and an appropriate increase in kinetic energy of the other.

As one might anticipate, if we characterize the kinetic energy of the electrons in the plasma by the temperature T_e, then the recombination of the electron with the ion is not permanent until the excited bound state reached is more than kT_e below the ionization continuum. The reason for this limitation is that inelastic collisions between other plasma electrons and the newly formed highly excited atom are quite likely and may result in re-ionization of the atom.

There are several ways of reaching the permanently recombined excited state. The initial interaction between two electrons and an ion may lead directly to capture into a sufficiently bound state; or the initial encounter may lead to capture into an excited state lying within kT_e of the ionization limit, and the electron may then radiatively decay to the lower excited state, or it may reach this lower state as a result of a superelastic collision with another plasma electron, with an attendant increase in the kinetic energy of this latter. Of the possibilities, the last, in which successive superelastic collisions with plasma electrons lower the excitation level to a permanently recombined state, is found to be the most important in the recombination process.

The effectiveness of plasma electrons in acting as third bodies in stabilizing the electron-ion process may be judged from the fact that, at $T_e = 300°K$, a concentration of only 10^9 electrons/cm^3 increases the recombination rate an order of magnitude above the two-body radiative value. Thus, three-body, electron-stabilized, electron-ion

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

recombination is expected to be of considerable importance in plasma devices, such as thermonuclear reactors, which typically run at electron concentrations of 10^{11} to 10^{15} electrons per cm^3 and at electron temperatures between 10^3 and 10^5 °K.

There is substantial agreement between experiment and theory concerning the rate of electron-stabilized recombination, but three-body electron-ion recombination involving a neutral atom or molecule as the stabilizing agent has not been investigated in any detail. However, simple arguments can be advanced which indicate that in this case, the disparate mass of the electron and atom, and the shorter range of the electron-atom interaction, lead to a considerable reduction in the recombination rate.

Let us compare the three-body recombination coefficients, $K(n_x)$, defined by the relation

$$\partial n_e/\partial t = -K(n_x)n_x n_i n_e \qquad \ldots.(3)$$

where n_e, n_i, and n_x are the concentrations of electrons, positive ions, and third bodies, respectively. At kinetic temperatures of ~300°K, the coefficient for electron-stabilized recombination is of the order of 10^{-19} cm^6 per sec, while the neutral-atom stabilized recombination is estimated to give a value of $\sim 10^{-26}$ cm^6 per sec, some 10^7 times smaller. One would therefore expect atom-stabilized three-body recombination to be of importance only in ionized media in which the concentration of neutral atoms approaches atmospheric values at sea level.

Processes in the ionosphere

If we now turn our attention to the ionospheric regions of the upper atmosphere, where very large electron-ion recombination rates have been inferred from a variety of observations [2], we find that the processes so far discussed are unable to account for the large loss of electrons by recombination. The ionospheric layers may be very approximately characterized by particle temperatures in the range 200–1000°K, electron and ion concentrations between 10^2 and 10^6 cm^{-3}, and neutral particle concentrations ranging from 10^9 to 10^{16} cm^{-3}. Thus, two-body radiative recombination is far too slow to explain the observed loss, and there are insufficient concentrations of either electrons or neutral molecules to cause the three-body processes to achieve the required electron-loss rates.

We are, therefore, led to inquire whether there is some two-body electron-ion recombination process in which a third body is, in effect, already present. If, instead of atomic ions X^+, there are molecular ions $(XY)^+$ likely to be present, then a highly effective two-body process—dissociative recombination—becomes possible. (We have used the symbols X and Y schematically to indicate actual atoms; thus, in the ionosphere one finds molecular ions such as O_2^+, NO^+, and N_2^+.)

The dissociative recombination process may be expressed as

$$(XY)^+ + e^- \rightleftharpoons (XY)^*_{\text{unstable}} \rightleftharpoons X^* + Y + \text{kinetic energy} \qquad \ldots.(4)$$

Here, a molecular ion captures an electron, without change of energy, to put the molecule into an unstable excited state. This state may either revert to the original condition—the process is called autoionization—freeing the electron, or it may dissociate into two atoms X and Y, at least one of which may be in an excited electronic state. If dissociation occurs, radiationless capture of the electron by the ion has been achieved.

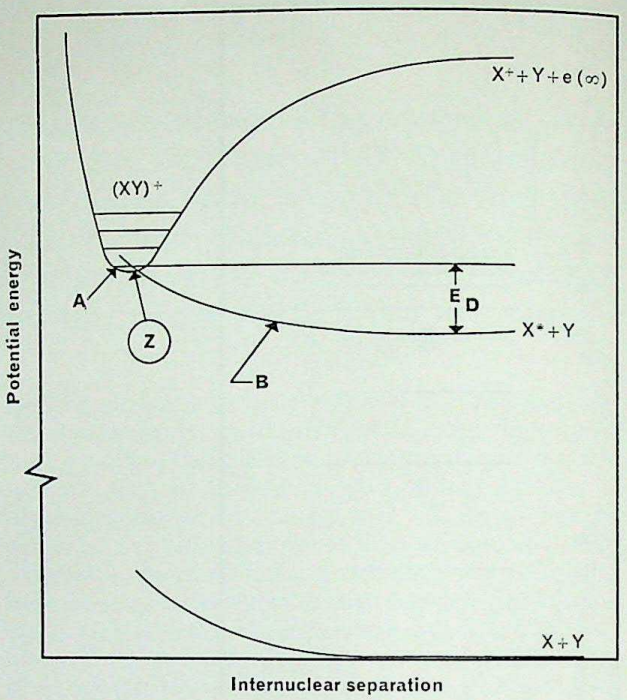


Figure 2 Representation of the potential energy between two atoms X and Y as a function of their internuclear separation for several possible states of the system. The curves are used to illustrate the process of dissociative recombination between electrons and ions.

The energetics of the dissociative recombination reaction may be better understood with the aid of figure 2, which exhibits the potential energy between two atoms X and Y as a function of their internuclear separation for several possible states of excitation. The stable molecule $(XY)^+$ results from the attractive interaction between X^+ and Y as they are brought together. The initial state of the system (A) indicates the molecular ion in its ground state of vibration with an electron at rest at infinity.

If the potential curves for this molecule are such that a repulsive state (B) of the excited molecule $(XY)^*$ crosses the molecular ion curve as shown, then the ion may capture the electron into this excited state without the emission of radiation or other change of energy of the system. The unstable molecule begins to dissociate, and if the internuclear separation increases beyond point Z before the electron is re-emitted, then autoionization is no longer energetically possible, and the dissociation goes to completion. This leaves the separated atoms X^* and Y. As a result of the repulsion between the atoms, they share the energy E_D as kinetic energy of dissociation.

In order to explain the ionospheric observations, the two-body dissociative recombination coefficient α_d, defined by

$$\partial n_e/\partial t = -\alpha_d n_i n_e \qquad \ldots.(5)$$

must be of the order of 10^{-7} cm^3 per sec, implying an electron capture cross-section of 10^{-14} cm^2 or larger. One can make qualitative theoretical arguments that the initial capture to form the unstable excited molecule (equation 4) may involve a cross-section of this size.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Further, the autoionization time may be long enough ($\geqslant 10^{-14}$ sec) to make dissociation into neutral fragments more probable than separation into the original charged particles. Thus, we estimate that dissociative recombination may be effective enough to provide the required large probability of electron capture. The reason for the vagueness in these statements is that present theoretical techniques are not sufficiently advanced to calculate quantitatively each step of the dissociative process and so arrive at an accurate prediction of the overall rate for the reaction.

Experimental techniques

Up to this point, we have discussed the various recombination processes largely in terms of theory and have not made clear the role of experiment in elucidating the recombination mechanisms and providing quantitative determinations of recombination rates. The dissociative recombination process, which is too complex to treat theoretically, provides an excellent example of a process that has been investigated successfully through a variety of experiments.

Some of the experimental techniques which have been applied to the study of recombination in ionized gases are indicated very schematically in figure 3. At the centre is the ionized gas under study. The free electrons in the gas interact strongly with microwaves to which they appear as a medium with a complex dielectric coefficient. This dielectric effect has been used to provide accurate measurements of the average electron concentration in the ionized gas. If measurements are made of the decay of electron concentration after the ionizing source is removed from the gas, then by comparing the time-dependence of the decay with the predictions of equations (3) or (5), it is possible to determine whether two-body or three-body recombination is occurring and to evaluate the appropriate recombination coefficient.

It is found that in laboratory studies of the afterglow periods of discharges in atmospheric gases—nitrogen and oxygen—and noble gases—neon, argon, and krypton—there is a very large loss of electrons by two-body recombination ($10^{-7} < \alpha < 10^{-6}$ cm^3/sec). There are a number of experimental tests which can be made to see if the dissociative process is responsible. Referring to reaction (4) it will be seen that three distinguishing features of dissociative recombination are:

1. Molecular ions are required.
2. If the ions are diatomic, then atoms are formed.
3. The atoms formed have a dissociation kinetic energy resulting from dissociation that is substantially greater than thermal energy.

The first point, the need for molecular ions, was first investigated indirectly. Fairly recently, it has been investigated directly using a mass spectrometer that samples the ions reaching the walls of the apparatus containing the ionized gas (figure 3). In microwave studies of electron-density decays in afterglows under conditions where first atomic ions, then molecular ions were expected to predominate, recombination loss was observed only in the latter case. The more recent mass-spectrometer studies of microwave afterglows in neon indicate that, when recombination is the predominant process, only Ne_2^+ ions are observed.

Inasmuch as the dissociative recombination is expected, in many cases, to lead to the formation of excited atoms, the second distinguishing feature of the process can be investigated by observations, with an optical spectrometer, of the radiation that accompanies the recombination. In the case of neon, when mass analysis indicates that the predominant afterglow ion is Ne_2^+, the afterglow spectrum consists only of neon lines. The intensity of these follows the decay of electron concentration in the manner that is to be expected if the recombination process is the source of this excited atom radiation.

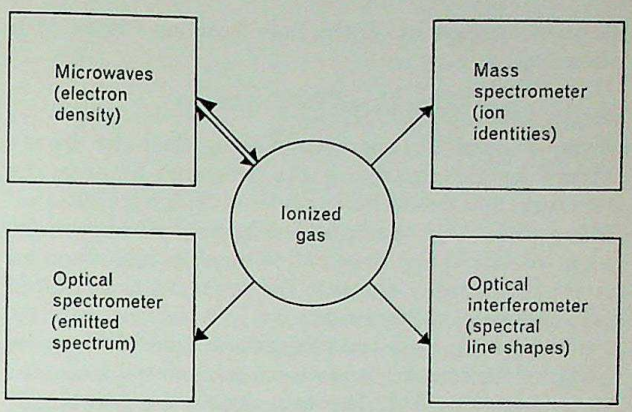


Figure 3 Experimental techniques used in investigations of recombination processes in ionized gases and their afterglows.

The third and most characteristic feature of the dissociative process—that the atoms formed have kinetic energies substantially in excess of thermal energy—can be studied by searching for the resultant Doppler shift in the radiation emitted by the fast excited atom. A detailed analysis of the expected spectral-line shape indicates that a substantially broadened flat-topped line should be observed.

Studies of the recombination radiation emitted from neon afterglows have been carried out using a photoelectric Fabry-Pérot interferometer. By the use of instruments of successively higher resolving power, it has been possible to observe the increased line-broadening and also the characteristic flat-topped line shape expected for a simple dissociative recombination reaction. Thus, it has been possible to elucidate the recombination mechanism observed in a certain class of laboratory studies and to determine accurately the associated two-body recombination coefficient.

It is difficult to determine the recombination coefficients in atmospheric gases because several species of molecular ions may be present. For example, in nitrogen, N_2^+, N_3^+, and N_4^+ are all stable ions, and in oxygen, O_3^+ as well as O_2^+ may be formed. By the simultaneous use of the experimental techniques indicated in figure 3, it is possible to determine the conditions in which recombination of electrons with a desired ion (such as N_2^+) is the dominant afterglow process, and so obtain quantitative measurements of recombination coefficients of ionospheric interest.

Ion-ion recombination

The significant processes by which a positive ion and a negative ion neutralize each other fall into two general categories, two-body mutual neutralization and three-body recombination in which a neutral molecule acts as

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

the stabilizing agent. If the basic reaction (figure 1) is written as

$$X^+ + Y^- \rightarrow X^* + Y + \text{energy}$$

where X^+ and Y^- are atomic ions, then the energy released by the reaction is the difference between the ionization and excitation energies of X, less the electron affinity of Y. (If either or both X and Y had been molecules, we should also have had to consider any vibration or rotation energy changes in the molecules as a result of their change of charge state.)

In three-body ionic recombinations, some of the excess energy of the reaction is imparted to a neutral molecule. Many years ago, J. J. Thomson proposed a very simple theory of three-body recombination that predicts reasonably well the values observed experimentally. The theory can be likened to one of planetary motion in a gravitational field involving the transition from an open (hyperbolic) orbit to a bound (elliptical) orbit.

If we consider a positive and a negative ion at large separation and with small kinetic energy of relative motion, then their total relative energy is a small positive quantity, since the potential energy resulting from their Coulomb attraction is essentially zero. As they move towards each other, the relative kinetic energy increases as a result of the decrease in potential energy. If nothing further happened, then the ions would pass each other and reach an indefinitely large separation. If, however, one ion collides with a third body, such as a neutral molecule, such that the total relative energy becomes negative, then the ions will execute closed orbits about one another. In Thomson's theory, it is assumed that this condition will last long enough for the ions to neutralize each other (presumably by electron transfer from the negative to the positive ion).

The probability of either the positive or the negative ion making a collision with a neutral molecule can be determined from the appropriate ionic mobility, which provides a measure of the desired collision cross-section. The Thomson theory leads to the prediction of a three-body ionic recombination coefficient in excess of 10^{-25} cm^6 per sec at 300°K. This rather large coefficient, which is in qualitative agreement with the only adequate experimental study made of the process, indicates that at very modest pressures ($\sim 10^{-2}$ atmospheres) and above, three-body ionic recombination provides an effective ion neutralizing mechanism.

Let us now consider an important two-body ionic recombination process, mutual neutralization. In this process, the energy released by the recombination appears as kinetic energy of the products, the neutral species X and Y. The process thus in some ways resembles dissociative recombination of electrons and positive ions. A moment's reflection indicates that, if $V_i(X)$, the ionization potential of X, exceeds $EA(Y)$, the electron affinity of Y, then at large separations the potential curve for the system $X^+ + Y^-$ lies above the curve for $X + Y$. Now, as a result of the long-range Coulomb attraction between X^+ and Y^-, the potential curve describing these particles decreases in value with decreasing separation between them. Since there is no corresponding strong, long-range attraction for the neutral atoms X and Y, the potential curves for the two states are likely to cross. We may make use of figure 2 to visualize this by considering that the uppermost curve now represents $X^+ + Y^-$. Starting essentially from rest at a large separation, X^+ and Y^- move towards each other under the attractive interaction. At the crossing point Z, the electron may transfer from the negative to the positive ion without change of energy of the system. If such transfer does take place, then neutral atoms moving with the same velocity as their charged counterparts will be formed. If $V_i(X)$ exceeds $EA(Y)$ by a sufficient amount, then many such potential curve crossings, involving various excited states of X, will occur, and neutralization may lead to formation of a number of electronically excited states.

Theoretical treatments [3] of mutual neutralization involving calculations of curve crossing and charge transfer probability have been carried out for such systems of ionospheric interest as $N^+ + O^-$, and $O^+ + O^-$. At 300°K the calculated mutual neutralization coefficients substantially exceed 10^{-8} cm^3 per sec, indicating neutralization cross-sections in excess of 10^{-13} cm^2.

Recently, there have been several attempts to study mutual neutralization experimentally by making use of a variation of the microwave technique which provides a measure of the electron-concentration decay from an initially ionized gas. The ion-decay studies are carried out using the dielectric interaction of the ions with a radio-frequency field to obtain absolute ion-concentration values; however, it is first necessary that essentially all of the free electrons in the ionized gas attach to neutral molecules to form negative ions, otherwise their strong interaction with the electromagnetic field obscures the ion interaction.

The systems $I_2^+ + I^-$ and $Br_2^+ + Br^-$ have been studied by this method, and the preliminary results suggest a value of the neutralization coefficient at 300°K which may be as large as 10^{-7} cm^3 per sec. Attempts are now in process to measure mutual neutralization between ions of ionospheric interest, such as O_2^+ and O_2^-.

Thus, although the first experimental studies of recombination between charged species date back to the end of the 19th century and the first attempts at theoretical descriptions are only slightly less venerable, the subject today is by no means exhausted. Although adequate experimental techniques for recombination studies require considerable care and ingenuity, many interesting studies of recombination processes, both theoretical and experimental, are currently under way. These are stimulated in some cases by the keen interest of ionospheric physicists and astrophysicists who wish to understand better the role of recombination processes.

References

[1] Massey, H. S. W. and Burhop, E. H. S. 'Electronic and Ionic Impact Phenomena.' Oxford University Press, London. 1952.

Bates, D. R. (Editor). 'Atomic and Molecular Processes.' Academic Press, New York. 1962.

Biondi, M. A. 'Atomic Collisions involving Low Energy Electrons and Ions,' in 'Advances in Electronics and Electron Physics', Vol. 18. Marton, L. (Editor), Academic Press, New York. 1963.

[2] Bates, D. R. and Massey, H. S. W. *Proc. roy. Soc., A*, 187, 261, 1946; *A*, 192, 1, 1947.

[3] Magee, J. L. *J. chem. Phys.* 8, 677, 1940.

Baulknight, C. W. and Bortner, M. H. 'Theoretical Calculations of Cross Sections of Importance to Atmospheric Deionization', Air Force Cambridge Research Laboratories Report No. AFCRL-64-142.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

The brittle fracture of steel

Digitized by Arya Samaj Foundation Chennai and eGangotri

L. Rotherham

Steel is usually considered to be a ductile material, and calculations of its strength under stress are based on this consideration. There have, however, been a number of examples of sudden failures where the metal behaved as if brittle, and where the crystals cleaved. This article discusses the nature of brittle fracture and some of the ways in which it can be predicted and avoided.

All engineering achievements depend on the availability of satisfactory materials of construction, and of these by far the most important are the ferrous alloys known as steels. The ascendancy of steel as an engineering material is much more recent than is often realized; about one hundred and twenty years ago the output of Britain, the world's largest producer, was 60 000 tons of steel each year, compared with 3 million tons of iron. Iron was the main engineering material of the early and middle years of the last century. Today the position is reversed, and the steel output of the United Kingdom will soon be 30 million tons per annum, compared with 3·5 million tons of iron.

The change was brought about initially by the invention, approximately a hundred years ago, of the Bessemer converter and the open hearth melting process, which each give a material whose properties are preferable to those of iron for many uses. Since then there has been constant development of improved processes and a rising demand for many special-purpose alloys. Low cost, availability, and special properties are the main reasons for the continuing predominance of steel.

Most of our existing steel production is still in the form of mild steel—of low carbon content—and low alloy steels, but for special purposes, such as those requiring high strength or resistance to corrosion, higher proportions of alloying elements such as chromium, nickel, manganese, and molybdenum may be needed.

In engineering practice, steel is generally regarded as ductile and therefore, unlike cast iron, not liable to brittle fracture; anyone whose car has been involved in an accident cannot fail to have been impressed by the ductility of the mild steel pressings used for the body-work. It may therefore seem strange that there should be any interest in brittle fracture of steels. However, the danger is real enough, as an example will show.

A practical case of a service failure from the electrical industry concerns a comparatively small turbo-generator that broke up following a fault that permitted the normal service speed of 3000 r.p.m. to rise to about 5000 r.p.m. As the centrifugal stressing increased two to three times, it is not surprising to find that the primary cause of the break-up was stress induced by gross overloading. Figure 1 gives a general impression of the havoc that occurred. A modern turbo-generator is a substantial and complicated assembly of castings and forgings, as can be seen from figure 2, which illustrates a 550 MW set. The turbine itself usually consists of a number of stages, with the blades carried on forgings, or on wheels shrunk on to the shaft, which is itself a large forging. The turbine is coupled to the alternator, which is generally made from a large cylindrical forging on which the copper windings are held, usually by non-magnetic retaining rings. As the electrical load on a modern alternator may exceed 500 000 horsepower, the failure of a component can have devastating results.

Enquiries into the failure in question revealed a number of interesting features. Figure 3 shows the state of the alternator forging when pieced together after the break-up. Metallurgists found three different modes of failure. Some of the breakages had the appearance of cleavage failures, that is, the crystals of the metal had cleaved; in others there were indications of ductile deformation; and in at least one other the failure began at a shallow fatigue crack. This crack may have promoted the first break in the forging, but whether this was because of the modification of the stress system due to the existence of the crack or whether the crack was merely an indication of the likely location of the highest stresses is a matter for speculation. What is clear is that apparently brittle failures may have occurred next to regions where the steel remained ductile. Figures 4 and 5, which were taken at the time of the accident, show the condition of two adjacent turbine wheels. The wheel in figure 4 was recovered bent but unbroken, but the adjoining wheel, shown in figure 5, showed ductile deformation of the bore and numerous brittle failures around. Metallurgically the interesting point about these two wheels is that the unbroken one contained a number of hairline cracks not found in the broken one, which suggests that the difference in behaviour probably depended on slight differences in their stress patterns. This supports the view that both the mechanics and the metallurgy of the fracture process are important.

The above example of a turbo-generator failure has made it apparent that brittle fracture is not the only mechanism by which steel can break. At least five such modes can be readily listed:

1. Brittle fracture.
2. Fatigue cracking.
3. Excessive macroscopic plastic deformation (ductile deformation).
4. Stress-corrosion cracking.
5. Excessive creep deformation.

In a turbo-generator, there are components which are at a sufficiently high temperature for creep deformation to be present, and it is not uncommon for stress-corrosion cracking to be observed in the non-magnetic steels used for retaining the generator windings. Three methods of failure may have been present in the failure that has been described—excess plastic deformation, cleavage fracture or brittle fracture, and fatigue cracking. If we add creep

L. Rotherham, *D.Sc., F.R.S.*
Was born in 1913 and educated at University College, London. In 1935 he joined Brown-Firth Research Laboratories and was appointed Head of the Physics Section a year later. From 1946 to 1950 he was Head of the Metallurgy Department of the Royal Aircraft Establishment, Farnborough, and he then became Chief Metallurgist at the Ministry of Supply's Division of Atomic Energy. He was later promoted to Director of Research and Development of U.K.A.E.A.'s Industrial Group at Risley. Since 1958 he has been at the Central Electricity Generating Board as Member for Research.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

deformation and stress-corrosion cracking, all five mechanisms of deformation and fracture may occur in abnormal conditions in a single turbo-alternator. Creep and ductile deformation are readily distinguished from brittle fracture, but stress-corrosion fracture and fatigue fracture may at first sight appear similar to brittle fracture. Before dealing with brittle fracture in more detail, it may be helpful to outline what is meant by stress-corrosion and fatigue.

Stress corrosion and fatigue

Stress-corrosion cracking is, of course, due to either a stress system, arising internally or externally, existing in a material, such as a stainless steel, which is exposed to an effective corrosive environment. A crack forms, which in the case of a stainless steel quite typically runs through the crystal grains and shows little sign of plastic deformation. Obviously either the stress or the corrosion may be severe enough to cause failure, but by stress corrosion it is usually implied that the combination of stress and corrosion leads to a more rapid failure than would either acting singly.

Although the crack formed may show little sign of plastic deformation, deformation is always present when metals are involved. Usually the stress is sufficient to cause a local deformation at a point of stress concentration which may arise mechanically or from local corrosive action. The effect of the deformation will be to set up, at the point of stress concentration, an electrochemical attack due to the potential difference between the deformed and undeformed areas. As a result, the already existing crack will deepen.

Similarly, the metal will sometimes fail when an alternating stress less than that of the macroscopic yield stress of the metal is applied for a prolonged period. This is known as metal fatigue, and when it occurs, it is certain that considerable plasticity, and perhaps local adjustment of stress on a local microscopic scale, occurs. Extensive metallographic studies have shown that the application of alternating stresses leads to alternating deformation concentrated in a few slip bands, regions apparently softer than their surroundings. These bands often form in areas where the effects of stress concentration exist. As the repeated stressing continues, ridges and grooves may form on the surface, and in certain cases material may appear to be 'extruded' from the slip bands. It is these slip bands that form into cracks that may appear very early in the life of the component. Not all cracks continue to grow—some are stopped by grain boundaries or by stress readjustments. Other cracks will grow steadily, and although the final stage of failure may be rapid, it is preceded by a lengthy process of plastic deformation that may continue up to the time of fracture.

Cleavage of the crystals is not an essential feature of either stress corrosion or fatigue, whereas the dramatic and sudden failure of structures under cleavage conditions such that the crystals cleave is one of the main features of brittle fracture.

Characteristics of brittle fracture

A great deal of attention was focused on the problem of brittle fracture by the breaking in two of a number of all-welded Liberty ships in the cold waters of the North Atlantic during the second World War. The disasters occurred under conditions where the applied stresses were not very high. In a riveted ship a crack in one plate would not normally progress into adjoining plates, and moreover a riveted joint permits slight movement between plates to give a measure of stress relief. The continuity of an all-welded structure makes it easier for a crack to propagate, and in addition involves the hazard that a crack may originate in a weld defect that forms a stress concentration.

Although the damage to the Liberty ships focused attention on the problem, there have been cases all over the world of road bridges, oil tanks, pressure vessels, turbine rotors, and many other structures failing by brittle fracture. However, the problem should not be exaggerated, for although very serious when it occurs, the percentage of structural failures that can be attributed to brittle fracture is minute.

The characteristics of a brittle fracture are as follows:

1. The surfaces of the crack are usually non-fibrous, and it appears, at least on a macroscopic scale, that little or no plastic deformation has taken place over the fracture surfaces.
2. The apparent stress at which failure takes place may be very low—much less than the measured ultimate tensile strength. In large structures, failure often occurs at stresses below the general yield stress. In this respect the turbo-generator failure already discussed was not a typical brittle failure, whereas the ship failures were.
3. The crack propagates very quickly—much faster than in the case of stress corrosion or metal fatigue.
4. The susceptibility of the material to brittle fracture is strongly dependent on temperature and other factors, such as the physical condition of the metal—its grain size and the type and concentrations of impurities it contains.

If it is assumed that the failure of an ideally brittle material is a process of forming two new surfaces, the work done will be equal to the energy of formation of the new surfaces. The separation of the two new surfaces may be said to have been achieved when the initial separation a of the atoms in the surfaces prior to failure has been increased by a suitable amount.

For a fracture stress σ_f under tension, the strain will be σ_f/E, where E is Young's modulus, providing the metal behaves elastically to the point of fracture, and the work done can be calculated and equated to the surface energy of the new surfaces. The simple equation resulting is

$$\sigma_f \simeq \sqrt{\frac{E\gamma}{a}} \qquad \ldots . (1)$$

where γ is the surface energy.

This may be considered an ideal fracture strength for a truly brittle material. We can substitute approximate values for γ in this equation, and ideal fracture strengths for real materials can be calculated on the assumption that they are brittle. The breaking strength in practice of a very strong steel, calculated on the assumption that the work done is equal to the energy of the newly-formed surface, is no more than about ten per cent of the ideal strength, and in glass for example the measured strength may not be more than one per cent of the value calculated on this basis.

Over 40 years ago, A. A. Griffith suggested [1] that the observed weakness of most materials was due to notches and cracks in the surface which act as stress raisers. If a

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

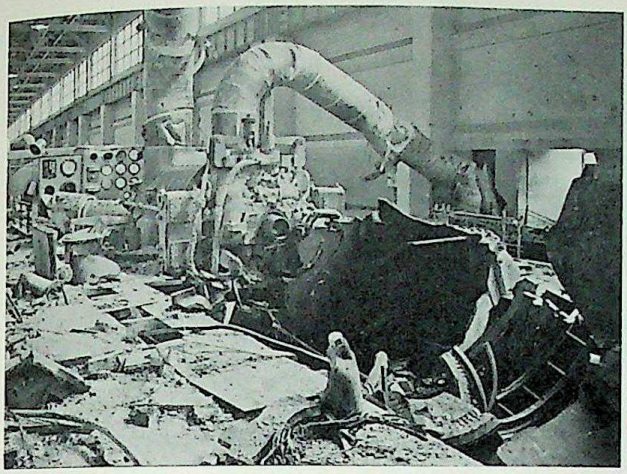


Figure 1 General view of the H.P. end of the turbo-generator with other debris after the breakdown.

crack is to grow, the energy of formation of the new surfaces must be provided by the energy released from the stress field of the crack, and by equating these two, a fracture stress

$$\sigma_m \simeq \sqrt{\frac{E\gamma}{c}} \qquad \ldots . (2)$$

is derived. We can see that the spacing between atoms, a of the previous expression, is now replaced by c, the crack depth. Since the measured strength σ_m is lower than σ_f by a factor of up to about 1000, the size of cracks necessary to give the observed change is considerable, and they ought to be observable in a suitable material. One such is glass, which is a reasonable approximation to a brittle solid.

In fact the existence of such cracks in the surface of glass was shown long ago by E. N. da C. Andrade and L. C. T. Tsien [2], and their technique of etching with sodium vapour has been widely used in further studies of crack formation on glass surfaces. If the cracked surface layer is removed, the glass becomes very strong—its strength rises to a limit of about $E/20$, an increase of about fifty times.

Griffith himself observed that freshly formed glass fibres are much stronger than old ones, and the conclusion from this is that older glass contains many more surface imperfections, as was shown by Andrade and Tsien. These surface faults are probably caused by the release of the stresses remaining in the glass after cooling and by atmospheric corrosion. These experiments prove that normally there are very fine cracks in the surface of glass, and a simple theory is available to show that it is then energetically feasible for failure to occur at stresses very much lower than the theoretical strength of the material. How these cracks can be prevented from occurring in a brittle manner in the range of new materials based on uncracked fibre elements—whiskers—was dealt with by J. E. Gordon [3] in a recent number of ENDEAVOUR. Unfortunately, the failure of a normally ductile metal in a brittle fashion is more complicated.

Deformation and fracture of a metal

The quality of a metal which in great measure accounts for the predominant importance of metals in engineering

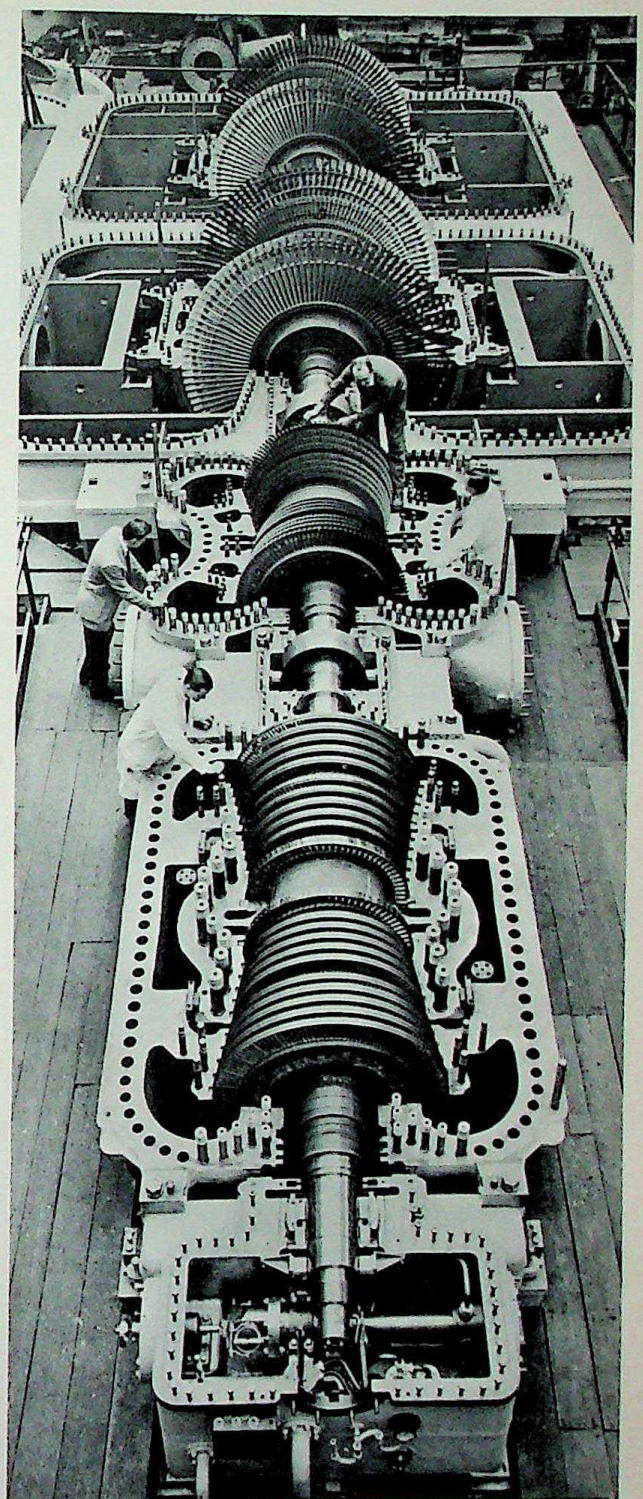


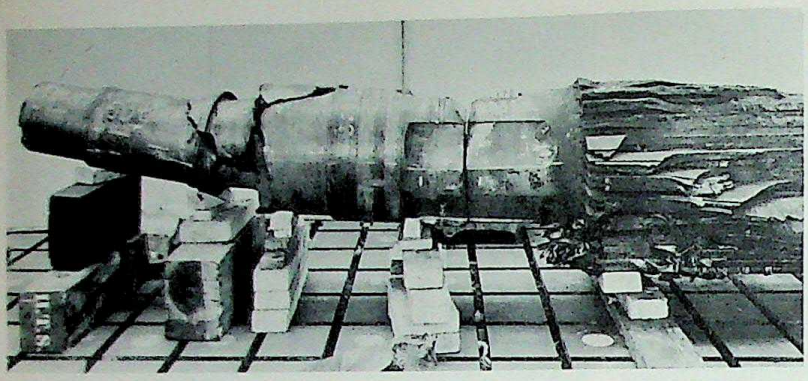
Figure 2 550 MW turbine under construction.

is of course the combination of strength with ductility. Ductility may in part be taken to mean the ability of the metal to readjust its shape to minimize the effects of stress concentrations. The energy considerations of Griffith's theory must be satisfied for a crack to spread, but these are made more complicated when plasticity permits large movements. It may be the case that considerable deformation can occur at low stresses, but the work done may still be high because the deformations are large.

The work of J. F. Knott and A. H. Cottrell [4] on

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

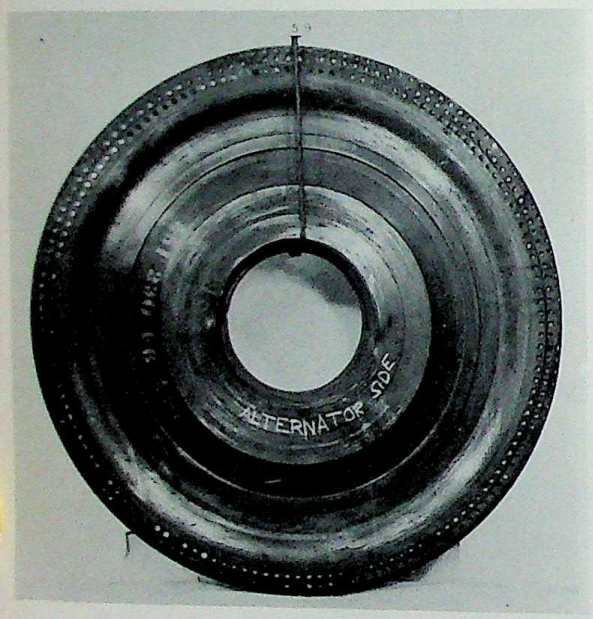


3

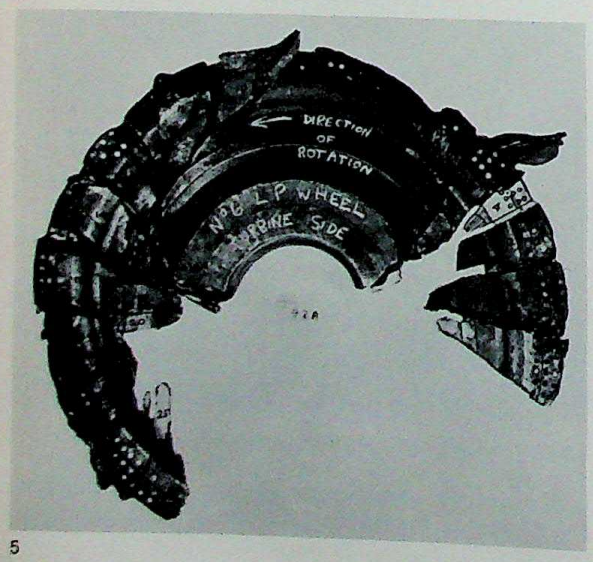
Figure 3 Alternator forging pieced together.

Figure 4 One low-pressure turbine wheel, bent but unbroken.

Figure 5 Low-pressure turbine wheel adjacent to that in figure 4.



4



5

notch brittleness in mild steel gives a good survey of the main properties of the fracture phenomena. Using notched specimens subject to stress in bending, with the notch in tension, the stress-concentration effect causes plastic deformation to occur first at the root of the notch. This plastic deformation has to be accommodated by yield zones spreading from the root of the notch and, providing yielding can continue, these zones will spread through the section as the load increases. If this occurs there will be general, as opposed to local, plastic yielding of the specimen and a relatively slow plastic failure.

For conventional mild steels at temperatures around o°C, fracture usually starts at the root of a notch where the strain concentration is a maximum and where the local plastic deformation must be accommodated by yield zones spreading across the section. If the critical amount of local deformation can be accommodated before these zones spread across the section, fracture will occur before general yield and there will be a low energy absorption.

Cottrell has shown [5] the effect of some variables on ductile–brittle transition effects by plotting the results of a number of workers (figure 6). Curve F represents the case of notches, as described in the preceding paragraphs; taking curve D as a further illustration, we see that a very similar effect arises from neutron irradiation. The case of temperature is made very precise by Knott and Cottrell's results as plotted in figure 7. It will be seen that, under the conditions of the experiment, general yielding with high energy absorption preceded fracture at high temperatures, but at lower temperatures, yielding would not have passed through the full cross-section of the specimen and parts of the fracture surface would show brittle cleavage fracture.

All these considerations show that failure in a ductile material can, in general, exhibit the characteristics of brittle fracture.

Effects of size

The data shown in figure 6 indicate that many factors affect the energy absorption at failure. All these are relevant to a consideration of the effects of size. Size effects are considered especially important, since many of the cases of brittle fracture of practical importance have occurred in large structures, such as ships.

A large object is statistically more likely to contain metallurgical defects, and generally it is more difficult to produce with satisfactorily uniform properties throughout the mass. More stress-concentration sites, and inferior properties, may be factors in the failure of large components, but there are also more fundamental reasons. It is necessary, as we have mentioned, for plastic zones to spread out from a notch so as to accommodate the local plastic strain at its root; if the local plastic strain necessary to cause fracture is attained before the

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

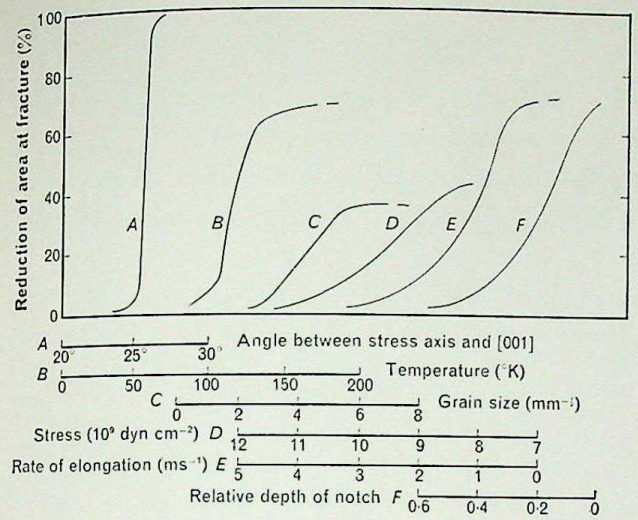

Reduction of area at fracture (%)
100
80
60
40
20
0
A
B
C
D
E
F
A 20° 25° 30° Angle between stress axis and [001]
B 0 50 100 150 200 Temperature (°K)
C 0 2 4 6 8 Grain size (mm⁻½)
Stress (10⁹ dyn cm⁻²) D 12 11 10 9 8 7
Rate of elongation (ms⁻¹) E 5 4 3 2 1 0
Relative depth of notch F 0·6 0·4 0·2 0

Figure 6 Brittle-ductile transitions in iron and mild steel: A, crystal orientation in single crystals, at 77°K; B, temperature, in polycrystals; C, grain size, at 77°K; D, initial yield stress of polycrystals, changed by neutron irradiation, at 77°K; E, rate of strain, at 144°K, of polycrystals; F, hydrostatic tension in stress state, as produced by increasing depth of notch, at 255°K, in polycrystals.

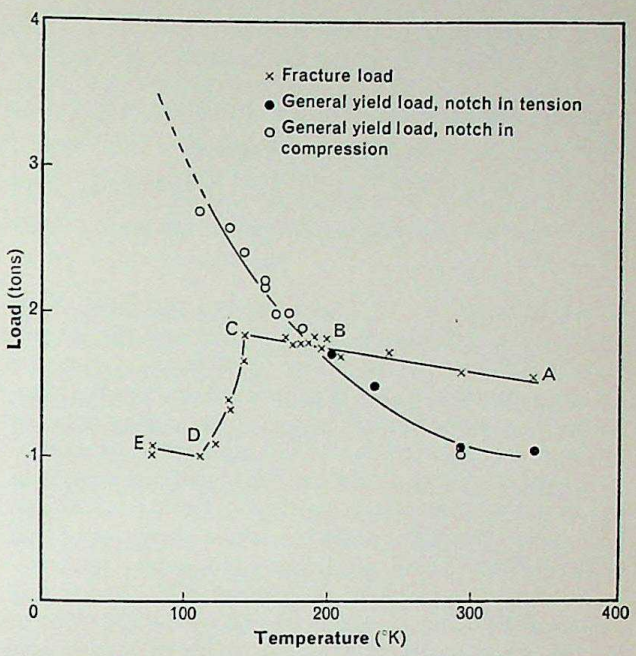


Figure 7 Loads for yield and fracture of notched specimens in bending at various temperatures.

zones spread across the structure, then fracture will occur before general yield. Thus there is a greater tendency for large structures to exhibit fracture before general yielding than small specimens.

Practical applications

Failures of artefacts by any mechanism are usually the result either of not applying existing knowledge, or, more rarely, of unjustified extrapolation of data. Conventional design procedure and inexact material specifications may be responsible for the neglect of existing knowledge. The rigid dependence of permissible stresses on the yield point of a material is an obvious example. It has been suggested by R. Weck [6] that in the design of pressure vessels, for instance, permissible stresses should not only be dependent on yield point but also take into account weldability and notch toughness at the appropriate temperature. This might be a start in the right direction, leading perhaps to a more rational design philosophy. The existing state of knowledge on brittle fracture suggests certain precautions which can be applied in the design and use of large steel components. A typical example might be the steel pressure vessel of a nuclear reactor.

By making observations on large samples as well as small, it will be possible to determine the effect to which size alone has introduced a proneness to brittle fracture. If, as in the case of the mild steel in Knott and Cottrell's work, the gap between yield strength and fracture strength increases markedly with temperature, the effect of increasing plate size and thickness will again be effectively to raise the temperature at which the transition from brittle to ductile failure can occur. This effect can easily be measured, and it would be prudent to do this and also to make sure that any reasonable variation in the speed of loading had little effect on the results. The steel selected for the measurements would preferably be well known, suitable for welding, and capable of being produced with a satisfactorily uniform grain size and adequate mechanical properties.

After a careful study of these matters, it should be possible to say that, above a certain temperature and having regard for the stress concentrations which are likely to occur, the vessel should behave in a ductile manner. In this case the energy absorption necessary for failure would not be available in the system and a sudden failure would be unlikely.

This concept of a minimum temperature is applied in nuclear operations and should give complete safety. Difficulties arise in applying this concept generally in other fields of engineering. When structures are operated below their crack-arrest temperature, this key safety factor disappears, and then the problem of fracture initiation must be seriously considered.

These very practical considerations of engineering importance, allied with the interesting background of active research into both the mechanics and metallurgy of fracture, will continue to attract attention for some years to come, since all the complexities of the subject have not been resolved. However, enough is already known to deal with most of the difficulties that can arise in engineering design.

References

[1] Griffith, A. A. *Phil. Trans.*, *A*, 221, 163, 1920.
[2] Andrade, E. N. da C. and Tsien, L. C. T. *Proc. roy. Soc.*, *A*, 159, 346, 1937.
[3] Gordon, J. E. *Endeavour*, 23, 8, 1964.
[4] Knott, J. F. and Cottrell, A. H. *J. Iron St. Inst.*, 201, 249, 1963.
[5] Cottrell, A. H. Bakerian Lecture, *Proc. roy. Soc.*, *A*, 276, 1, 1963.
[6] Weck, R. 'Failure of Steel Structures: Causes and Remedies.' Paper to Royal Society, 28 May 1964.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

The ribonucleic acids in the nucleus and cytoplasm of animal cells

Digitized by Arya Samaj Foundation Chennai and eGangotri

Henry Harris

During the last decade, the number of papers dealing with the behaviour of ribonucleic acids in the cell has undergone an explosive increase. New techniques have been evolved and new interpretations of well-known data advanced. This article discusses the function of the RNA in the nucleus and cytoplasm of animal cells and indicates some of the problems arising from recent studies.

In 1950, when T. O. Caspersson, in his book 'Cell Growth and Cell Function' [1] put forward the general view that RNA was the vector of information from the chromosomes to the sites of protein synthesis in the cytoplasm, it was not thought that the relationship between nuclear and cytoplasmic RNA presented any special problems. Caspersson's observations were consistent with the view that there was a continuous flow of RNA from nucleus to cytoplasm; and while it was not excluded that some of the RNA in the nucleus might play an intranuclear role, the bulk of the nuclear RNA was simply regarded as RNA in transit to the cytoplasm. Recent studies have suggested that the RNA in the nucleus contains a number of components which may have different physiological roles. The study of the relationship between these nuclear components and the ribonucleic acids in the cytoplasm has raised problems of great complexity.

Nuclear ribonucleic acid

The amount of RNA in the cell nucleus and its distribution

In animal cells, 15 per cent or more of the RNA in the cell may be found in the nucleus. The amount of nuclear RNA bears no constant relationship to the amount of DNA in the cell, and in a given individual may vary from one cell type to another. Within one cell type, changes in the amount of nuclear RNA may be produced by changes in physiological function. The RNA is distributed over all the chromosomes and is also to be found in the nucleolus. In cells in which the nucleoli are well developed, most of the nuclear RNA may be found in these structures.

The distribution of RNA on the chromosomes has been most thoroughly studied in the giant chromosomes of cells of the glands of certain insects. In general, the individual chromosomes are not discernible in the somatic cells of animals except during mitosis, the stage of cell division, but in these specialized glandular cells of insects the individual chromosomes can be seen as discrete structures during other stages of the cell cycle. Their large size is due to the fact that they are polytene, a condition in which the chromosome contains high multiples of each chromosomal strand associated in parallel. Polytene chromosomes show a large number of transverse bands, in which many individual genes have now been located. The RNA is found along the whole length of the chromosomes, but it is not evenly distributed. Accumulations of RNA of various size are found in association with the transverse bands, and these accumulations are referred to as 'puffs'; the largest of them are sometimes called Balbiani rings. One view of the nucleoli is that they are themselves giant puffs associated with specific genetic loci (figures 1 and 2).

The pattern of puffing appears to be specific for each particular cell type, and in any one cell type it may vary with different physiological states. Changes in the puffing pattern can be induced by changes in temperature and by the administration of certain hormones. It is generally considered that the formation of a puff at a given locus represents an increase in the state of activity of the genes at that locus, and conversely the disappearance of a puff is thought to represent a diminution of gene activity. We have little information about the mechanism by which puff formation is induced, but it appears to involve some localized loosening or unwinding of the secondary coiling of the chromosomes. There is little doubt that the puffs are formed by the synthesis of RNA at the loci involved. Exposure of the cells to a labelled RNA precursor results in labelling of the chromosomes in a manner that exactly reflects the distribution of the RNA (figure 3).

A variable amount of RNA is found in the so-called 'nuclear sap' fraction. This is a fraction usually extracted from isolated nuclei by phosphate buffer, but there is evidence that in somatic animal cells, most, if not all, of this fraction represents cytoplasmic contamination [2].

Physical characteristics of nuclear RNA

With the possible exception of the ill-defined RNA in the nuclear sap fraction, very little, if any, of the nuclear RNA is found free in solution. The studies so far undertaken indicate that the RNA in the nucleus is present in some form of association with protein, and much of it appears to be attached to the chromosomes themselves or to some structural components of the nucleolus. The precise nature of the attachment of RNA to these structures has not yet been established, but protein appears to be involved: the RNA can be released from the chromosomes by procedures that remove the protein. There is some evidence that the protein associated with RNA in the puffs of polytene chromosomes is not all synthesized at the same time as the RNA itself; it appears that some pre-formed protein becomes attached to the newly formed RNA [3].

It is generally found that, under conditions designed to minimize degradation, most of the RNA that can be extracted from cell nuclei sediments as two components having sedimentation coefficients of about 28 s and 16 s (s=a svedberg, the unit of sedimentation velocity in a field of unit acceleration) [4, 5]. If certain assumptions are made about the structure of this RNA, these sedimentation coefficients correspond to molecular weights of about $1{\cdot}3 \times 10^6$ and $6{\cdot}5 \times 10^5$ respectively. When cells are exposed for a few minutes to a radioactive

Henry Harris, *B.A., M.B., B.S. (Syd), M.A., D.Phil. (Oxon)*

Was born in 1925 and educated at the Sydney Boys' High School and Sydney University. After a period of research at the Sir William Dunn School of Pathology, Oxford, and the National Institutes of Health at Bethesda, Maryland, he became the Head of the Department of Cell Biology at the John Innes Institute. In 1963 he was appointed to the Chair of Pathology at Oxford.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

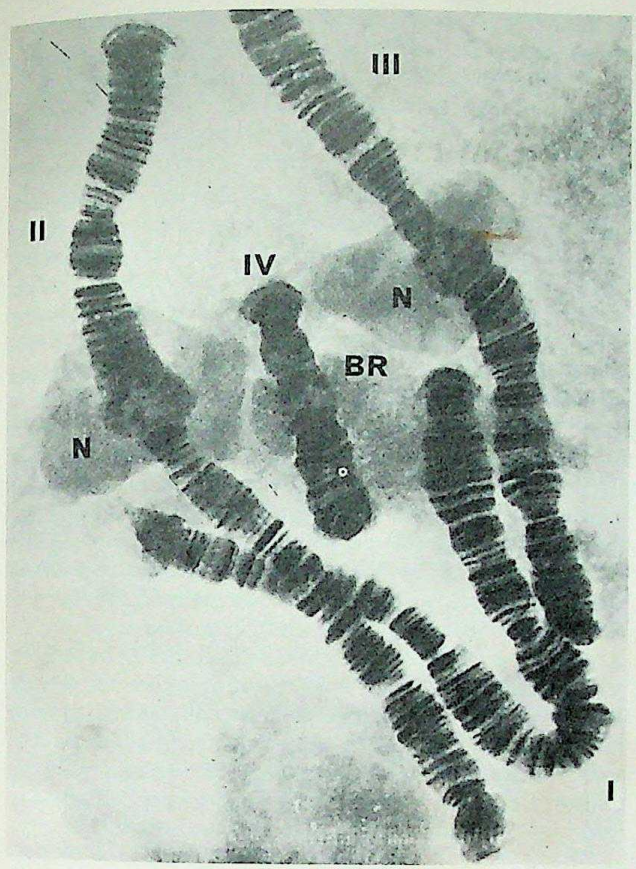


Figure 1 The polytene salivary gland chromosomes (I, II, III, IV) of *Chironomus tentans.* The nucleoli (N) and a large puff (Balbiani ring) (BR) are shown. (×550)

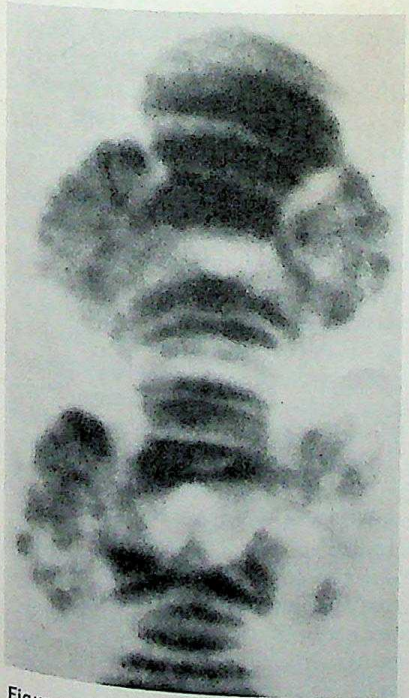


Figure 2 Two large puffs (Balbiani rings) on chromosone IV of the salivary gland of *Chironomus tentans.* (×2750)

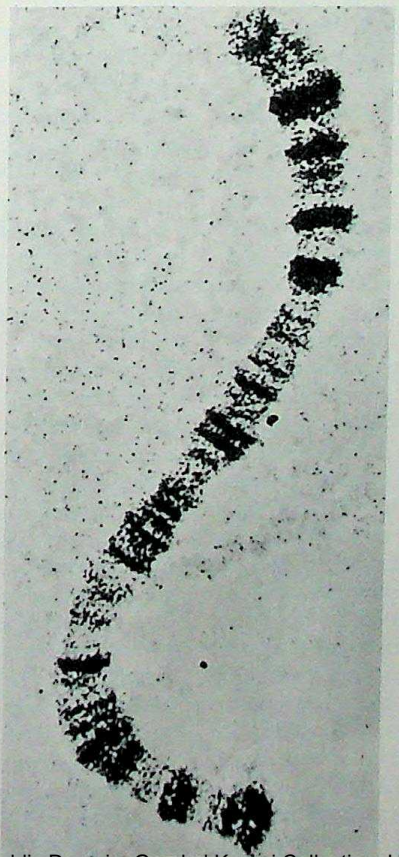


Figure 3 Autoradiograph of chromosome I of *Chironomus tentans.* The salivary gland cells were exposed for 6 hours to tritium-labelled uridine, which is readily incorporated into RNA. The black grains over the chromosome indicate the sites at which the labelled RNA precursor was incorporated. (×800)

RNA precursor, and the sedimentation behaviour of the nuclear RNA is measured by the distribution of radioactivity in sucrose density gradients, minor components are sometimes found which contain a large proportion of the radioactivity and which have very heterogeneous sedimentation properties [5, 7]. The relationship between the 28 s and the 16 s components, and the significance of these minor, rapidly labelled, components, are discussed later in this article.

Soluble RNA in the nucleus

The cytoplasm of almost all animal cells contains a variable amount of RNA which has a sedimentation coefficient of about 4 s. This group of RNA molecules is generally called either 'soluble' RNA, because of its low sedimentation coefficient, or 'transfer' RNA, because it has been shown that it will accept activated amino acids as an early step in the synthesis of protein. Soluble RNA characteristically contains pseudo-uridylic acid and sometimes other unusual nucleotides. Whether the nucleus contains appreciable amounts of 4 s RNA is a vexed question. Quite large amounts of this RNA have indeed been found in the nuclei of thymus cells, but it has been suggested that these nuclei are seriously contaminated with cytoplasm. Recent studies on the nuclei of HeLa cells, a strain of human cells maintained in artificial culture [4], and liver nuclei [8] have failed to reveal any large amount of 4 s RNA. Some workers have detected a component which sediments at about 6 s [6] but it is likely that this is a breakdown product of the 28 s and 16 s components. The amount of pseudo-uridylic acid present in the RNA of liver nuclei isolated under the most carefully controlled conditions suggests that the amount of soluble RNA present in these nuclei does not exceed 5 per cent of the total amount of nuclear RNA [8].

Nuclear ribosomes

Three-quarters or more of the RNA in the cytoplasm of animal cells appears to be present in ribonucleoprotein particles. These particles are commonly called ribosomes, and most of the protein synthesis that occurs in the cytoplasm is thought to take place on these structures. Whether ribosomes are present in the nucleus is uncertain. Electron micrographs do indeed show grains in the nucleus having the approximate dimensions of cytoplasmic ribosomes and showing, like the latter, an affinity for heavy metals. But there is no way of distinguishing in electron micrographs between particles in the nucleus and strands of chromatin cut in

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

cross section. Ribonucleoprotein particles can be extracted from isolated nuclei by buffers and salt solutions, but these particles have very heterogeneous sedimentation properties, and there is some question as to whether they might not in fact be produced by the extraction procedure itself. Evidence obtained from the fractionation of the RNA-containing material found in isolated liver nuclei suggests that what are termed nuclear ribosomes might really be fragments of chromatin [2, 8]. When nuclei isolated from some cells are expanded by treatment with hypotonic solutions, the chromatin network is loosened, and although such nuclei are known to contain their normal complement of RNA, structures corresponding to ribosomes are not seen [9]. Nor can ribosomes like those found in the cytoplasm be produced from such isolated nuclei by standard methods. It is thus possible that structures corresponding to cytoplasmic ribosomes might be present in the nucleus only in very small amounts. A detailed autoradiographic study of nuclear protein synthesis in animal cells suggests that this takes place on, or in close association with, the chromosomes themselves [10]. If ribosomes are involved in this synthesis, it seems likely that they would have to be closely associated with the chromatin.

Base composition of nuclear RNA

The most detailed study of the base composition of nuclear RNA is that made by J.-E. Edström and his colleagues on the salivary gland cells of *Chironomus* [11]. Using a micro-electrophoretic technique, these workers succeeded in measuring the base composition of the RNA in individual nucleoli and chromosomes, and even in single chromosomal puffs. These structures were isolated by micro-dissection from nuclei fixed in buffered formalin. Since the RNA was precipitated by the fixation, there was little risk of its being degraded during the isolation procedure. It was found that the base composition of the nucleolar RNA resembled the overall base composition of the RNA in the cell cytoplasm. This resemblance has been adduced as evidence for the view that the cytoplasmic ribosomal RNA is derived from the nucleolus. The ribonucleic acids attached to different chromosomes had different base compositions, and the base compositions of the ribonucleic acids in individual puffs of a single chromosome also varied. In any one puff, the RNA did not have a base composition resembling that of the DNA at that locus, and it did not show base symmetry: that is, the amount of adenine was not equal to the amount of uracil nor the amount of guanine to that of cytosine, as is the case with DNA (substituting thymine for uracil). These findings suggest that the RNA made at any particular locus on the chromosome is not a copy of both strands of all or part of the DNA of that locus; and since the base composition of the RNA made at one locus may differ markedly from that at another, it appears that the base composition of the fraction of DNA on which the RNA is made may also differ from one locus to another. The obvious heterogeneity of the base composition of the nuclear RNA at different sites on the chromosome makes it very unlikely that any great biological significance attaches to the fact that certain essentially arbitrary chemical procedures extract from the nucleus as a whole a fraction of RNA having a base composition showing some resemblance to the base composition of the DNA as a whole.

Cytoplasmic ribonucleic acid

There are two main classes of RNA in the cytoplasm: the soluble, or 4 s, RNA, which has been defined above, and the 'ribosomal' RNA.

Soluble RNA

Each molecule of soluble RNA contains about 80 nucleotides. When this RNA is extracted from the cell it has, under certain conditions, a high degree of secondary structure: most of the molecule appears to be a double helix with the two strands apparently paired by hydrogen-bonding in much the same way as in DNA. There is evidence that the unusual nucleotides, such as pseudouridylic acid, that are characteristic of soluble RNA, are found in the terminal loop of the molecule where helix formation is thought not to be present. Whether soluble RNA has so ordered a structure in the intact cell is not known. Although there are only 20 or so amino acids, there appear to be at least 50 molecular species of soluble RNA, as judged by their ability to accept individual activated amino acids: certain amino acids can apparently be accepted by more than one species of soluble RNA. Some of these species of soluble RNA have been partially purified, and it has been shown that the soluble RNA which accepts one amino acid contains some sequences of nucleotides different from those in the soluble RNA which accepts another. In animal cells, the soluble RNA as a whole has a high content of guanine and cytosine.

Ribosomal RNA

Although it is possible that small amounts of RNA are present as components of cytoplasmic membranes, and perhaps also of some other organelles such as mitochondria, most of the high molecular weight RNA in the cytoplasm appears to be contained in ribonucleoprotein particles or ribosomes. The properties of ribosomes isolated from animal cells depend to some extent on the tissue from which they are derived, on the method of preparation, and on the physical conditions under which they are examined. They appear to consist of about 50 per cent RNA and 50 per cent protein. They are often obtained from a single tissue as two or more groups having sedimentation coefficients ranging from 80 s to 40 s. In electron micrographs of fixed cells they appear as fairly uniform structures about 150 Å in diameter.

The distribution of these particles in the cytoplasm is of some interest. In cells actively engaged in the secretion of protein, such as those of liver, pancreas, or mammary gland, most of the ribosomes are attached to an extensive membrane system, the endoplasmic reticulum. The ribosomes are attached to this membrane in a single layer, and each ribosome is closely surrounded by its neighbours. The endoplasmic reticulum is thus studded with a regular array of single ribosomes (figures 4 and 5). The ribosomes are attached quite firmly to the membranes, and rather drastic procedures are necessary to detach them. One such procedure is to treat the cell with sodium deoxycholate; this lyses the membranes and releases the ribosomes, some of which may then be obtained in solution as clusters. It has been shown that in liver cells most of the protein synthesis in the cytoplasm takes place on the ribosomes attached to the endoplasmic reticulum. The unattached ribosomes appear to play a minor role in this connection and only a small proportion of them are

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

extracted from the cell as clusters. In cells that do not have an extensive cytoplasmic membrane system, most of the ribosomes are thought to be free in the cytoplasm. Electron-micrographs of such cells may show the ribosomes to be present both as single units and as clusters containing from 2 to 50 or more such units. When clusters of ribosomes are isolated from the cell, the aggregates can be broken up by very slight digestion with ribonuclease. This has been taken to indicate that the ribosomes are held together by a strand of RNA, although the effect could result from the removal of some of the ribosomal RNA from the surface of the ribosomes. It is also possible that RNA which was not attached to the ribosomes in the intact cell might become attached to them during the procedures used for their preparation. There is at present no conclusive evidence that the clusters of ribosomes seen in the intact normal cell are held together by a strand of some special form of RNA, or that a strand of this sort is involved in the functioning of the ribosomes attached to the membranes of the endoplasmic reticulum.

Physical characteristics and base composition of ribosomal RNA

After extraction from the cell, the ribosomal RNA, like the nuclear RNA, usually separates in the ultracentrifuge as two components having sedimentation coefficients of 28 s and 16 s. It has been clearly shown that the proportion of these two components in ribosomal RNA from a single source depends on the method of extraction of the RNA, the ionic strength and temperature of the extraction medium, and the concentration of divalent cations [12]. In any one preparation a high yield of the 28 s component is usually accompanied by a low yield of the 16 s component, and *vice versa*. It has therefore been suggested that the 28 s component is a dimer of the 16 s, or alternatively that the latter is the result of breakdown of the former. Under certain physical conditions some of the ribosomal RNA may be obtained as a component or components with sedimentation coefficients greater than 28 s. It is likely that these are complexes of the 28 s or 16 s components.

This view of the interrelationship between the 28 s and the 16 s components of ribosomal RNA appears to be at variance with two other observations. Firstly, the base compositions of the two components appear to be slightly different [13]. Secondly, the two components do not appear to compete for the same sites when they are 'hybridized' with DNA [14]. Hybridization is carried out by mixing a preparation of RNA with a preparation of denatured DNA under certain specified conditions: complexes of DNA and RNA are formed, some of which resist digestion with ribonuclease. Such ribonuclease-resistant complexes are thought to represent specific regions of RNA and DNA united by complementary base-pairing. The fact that the 28 s and 16 s components of the ribosomal RNA do not appear to hybridize with the same fraction of the DNA is therefore taken to mean that the two components are made at different genetic loci.

This discrepancy is of great theoretical importance. Until recently, it was generally thought that the specifications for the synthesis of cytoplasmic proteins resided in the ribosomal RNA. In 1961, however, a theory was put forward which did not assign this role to the ribosomal RNA. It was contended that ribosomal RNA was 'non-specific' and that specificity was conferred upon it by the attachment of a special form of RNA, to which the name 'messenger' was given [15, 16]. The ribosomal RNA was thought to be made on relatively few genes and to be essentially the same in different cell types. This view was supported by experiments which showed that ribosomal RNA hybridized with only a very small fraction of homologous denatured DNA [17]. But if it is true that the 28 s and 16 s components represent different states of the same set of molecules, the fact that these components do not compete for the same sites when they are hybridized with DNA raises doubts about the precise significance of DNA-RNA hybridization experiments as a whole.

The base composition of ribosomal RNA is indeed rather similar in many animal tissues: it usually has a high content of guanine and cytosine. This gross similarity is not very surprising, since the overall amino acid composition of the proteins of most animal tissues is also rather similar. Recent studies appear to show, however, that there are distinct differences in the base composition of ribosomal RNA in different tissues of a single animal, and also that the base composition of the ribosomal RNA in any one tissue is characteristically similar in different animal species [18]. It is, moreover, clear that ribosomal RNA from a single cell type is by no means a homogeneous collection of molecules. If it should prove that ribosomal RNA is a mixture of a very wide spectrum of different molecules, and that the mean base composition of this mixture is characteristically different in different tissues, it would be difficult to maintain either that the role of ribosomal RNA was 'non-specific', or that it was made on relatively few genes. Whether, in normal animal cells, the specifications for the synthesis of specific proteins are carried by the ribosomal RNA or by some other form of RNA is at present an open question.

Minor components detected by radioactive labelling

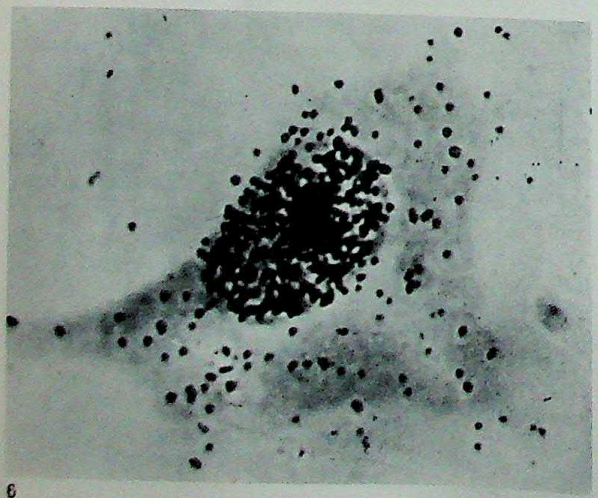
When cells are exposed for a short period of time to a radioactive RNA precursor, and the RNA is then fractionated by density gradient centrifugation in sucrose, trace components are found which, under certain conditions, separate in the ultracentrifuge in positions different from the main 28s, 16s, and 4s components. These trace components are usually present in amounts too small to permit isolation and chemical characterization, but they may contain a large proportion of the radioactivity. They show very polydisperse sedimentation behaviour, but may after certain extraction procedures separate largely as heavy components with sedimentation coefficients of 35 s or 45 s [7]. They are usually found only in the nuclear RNA. The significance of these components is at present a matter of controversy. It has been variously contended that they are the specific vectors of information from the genes to the cytoplasmic ribosomes, that they are precursors of the ribosomal RNA, and that they fulfil both roles. On the other hand, it is possible that they are simply complexes of partially degraded RNA. It is known that the newly formed RNA in the cell is extremely susceptible to degradation [4] and it would therefore not be surprising if, after a short period of exposure of the cells to a radioactive RNA precursor, much of the labelled RNA were extracted in a partially degraded condition.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

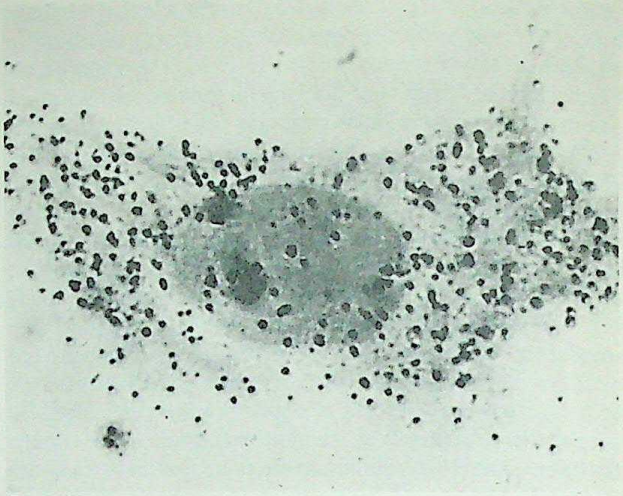
Digitized by Arya Samaj Foundation Chennai and eGangotri

4

5



6



7

Figure 4 Cross section of the endoplasmic reticulum of a cell from the lactating mammary gland of a rat. The ribosomes, shown as dark dots, are attached to the membranes of the reticulum as a single layer. This is clearly seen at the sites shown by the arrows. (×51 000)

Figure 5 Section from a 'plasma cell' in the lymphatic tissue of the gut of a mouse. Such cells are thought to be engaged in the secretion of antibodies. The arrows show parts of the endoplasmic reticulum sectioned *en face*. It can be seen that the membranes are studded with a close-set array of single ribosomes. (×38 000)

Figure 6 Autoradiograph of a rat connective tissue cell grown on a glass surface. The cell was exposed for 20 minutes to tritium-labelled adenosine, which is readily incorporated into RNA. The distribution of the grains indicates that most of the labelled precursor was incorporated into the RNA in the cell nucleus. (×500)

Figure 7 Autoradiograph of a rat connective tissue cell that was exposed for 20 minutes to tritium-labelled adenosine and then maintained for 12 hours in non-radioactive medium. The distribution of the grains indicates that most of the radioactive precursor is now in the cytoplasmic RNA. (×500)

Polydisperse rapidly labelled components in the cytoplasm of some cells have also been described, although here they are generally found to have rather low sedimentation coefficients, 8 s to 12 s. Such components may be found when the cells are homogenized and ribosomal preparations are made [19, 20], but they are not found when the cytoplasmic RNA is extracted directly from the cells by treatment with phenol in the absence of detergents [21, 22]. It is therefore possible that these polydisperse cytoplasmic components represent partially degraded RNA emanating from damaged nuclei or other cell components.

Clearly, a great deal of careful work will be necessary to elucidate what, if any, biological significance these trace components possess.

The relationship between nuclear and cytoplasmic ribonucleic acid

It has been known since 1948 that when animal cells are exposed to a radioactive RNA precursor, the RNA in the cell nucleus becomes labelled much more rapidly than does the RNA in the cytoplasm [23]. When cells labelled in this way are transferred to non-radioactive media, radioactivity gradually disappears from the nuclear RNA

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

and, under certain circumstances, appears in the cytoplasmic RNA. This observation has been made repeatedly in many cell types with a variety of techniques. Figures 6 and 7 illustrate an experiment of this sort carried out by autoradiographic methods on connective tissue cells labelled with tritiated adenosine.

The redistribution of radioactivity seen in this sort of experiment was originally interpreted as a demonstration of the transfer of labelled RNA from nucleus to cytoplasm. Subsequent work has revealed that the passage of radioactivity through the cell under these conditions is a process of great complexity, and there is now no unanimity of opinion about the precise significance either of the loss of radioactivity from the nuclear RNA or its appearance in the cytoplasmic RNA.

Evidence has been presented in support of the view that much of the rapidly labelled RNA in the nucleus is involved in a process of intracellular turnover, that is to say, it is being continuously made and broken down within the cell [24]. This appears to be the case both for multiplying [25, 4] and non-multiplying animal cells [26] studied *in vitro*, and for cells growing exponentially *in vivo* [27]. A good deal of work has been done to determine whether this rapidly labelled nuclear RNA is transferred to the cytoplasm before being broken down, or whether it is broken down within the nucleus. This problem has not yet been resolved in detail, but the present evidence appears to indicate that the breakdown takes place largely within the nucleus [4, 28]. The enzyme or enzymes apparently responsible for the breakdown are of a special type. They act only on RNA, not on DNA; they degrade the RNA sequentially from the ends of the polynucleotide chains; and they release 5′ mononucleotides, not 2′, 3′ nucleotides such as are released by the action of the common ribonucleases of the pancreatic type [4, 29]. The ribosomal RNA in intact ribosomes and the soluble RNA appear to be relatively insusceptible to the action of these enzymes [4].

The biological significance of this apparently intranuclear RNA turnover remains obscure. There is reason to believe that in differentiated somatic cells only a small fraction of the RNA made on the genes is transferred to the cytoplasm to serve as a template for protein synthesis [30]. Some recent experiments suggest that some selective mechanism, perhaps involving the firm attachment of protein, stabilizes this fraction of the nuclear RNA and shields it from the action of the intranuclear degradative enzymes; these break down the RNA not shielded in this way [31]. This idea implies that in animal cells the templates for the synthesis of protein are transferred to the cytoplasm as essentially stable molecules. There is now a substantial body of evidence indicating that this is indeed so. The production of more RNA than is actually used for the synthesis of proteins appears at first glance to be a rather wasteful process; but it is not difficult to give reasons why an overproduction of RNA might be necessary or to see how a selective mechanism operating on this overproduction might confer biological advantages on the cell.

When cells are exposed to a radioactive RNA precursor, the soluble RNA in the cytoplasm becomes labelled before the ribosomal RNA and the 16 s component of the latter before the 28 s component [4]. If the cytoplasm does not possess the ability to synthesize RNA, then the appearance of radioactivity in these cytoplasmic RNA components could provide some information about the flow of RNA from the nucleus. But if synthesis of RNA also takes place in the cytoplasm, any analysis of the incorporation of radioactivity into cytoplasmic RNA components is beset with formidable difficulties.

Whether the cytoplasm of higher cell forms has the ability to synthesize RNA is a question about which opinion is at present divided. There are those who believe that all the RNA in the cell is made in the nucleus—a view supported by certain experiments with the antibiotic actinomycin D [32]; by some studies involving enucleation of cells [33, 34]; and by the failure so far to reveal in the cytoplasm of normal cells a specific enzyme capable of synthesizing RNA on a template of RNA. On the other hand, it has been shown that amoebae from which the nucleus has been removed can incorporate radioactive precursors in an apparently normal way into both the soluble and the ribosomal RNA in the cytoplasm [35]; net synthesis of RNA has been demonstrated in the giant unicellular alga *Acetabularia* after removal of the nucleus [36]; and incorporation of precursors into RNA has been demonstrated in both animal [37] and plant cells [38] during those stages of mitosis in which synthesis of RNA on the chromosomes is thought to be suspended.

The resolution of this question is of crucial importance. If the cytoplasm of the cell has the ability to replicate the templates for protein synthesis, it could respond to external stimuli by increasing the number of protein synthesizing units, and different units might be replicated in response to different stimuli. If, however, the cytoplasm cannot synthesize RNA and is thus merely the receptacle of RNA made in the nucleus, all such regulatory responses must operate through the nucleus. Many aspects of cellular physiology will not be adequately understood until we know the answer to this question.

Acknowledgments

Figure 1 is reproduced by courtesy of Drs J.-E. Edström and W. Beermann and the editors of the *Journal of Cell Biology*, and figure 2 by courtesy of Dr U. Clever and the editors of *Chromosoma*. Figure 3 was kindly supplied by Dr C. Pelling of the Max-Planck-Institut für Biologie, Tübingen, and figures 4 and 5 by Dr G. I. Schoefl of the Sir William Dunn School of Pathology, Oxford.

References

[1] Caspersson, T. O. 'Cell Growth and Cell Function', W. W. Norton & Co. Inc. New York, 1950.
[2] Maggio, R., Siekevitz, P., and Palade, G. E. *J. Cell Biol.*, 18, 267, 1963.
[3] Beermann, W. Jenkinson Memorial Lecture, University of Oxford. 1963.
[4] Harris, H., Fisher, H. W., Rodgers, A. L., Spencer, T., and Watts, J. W. *Proc. roy. Soc., B*, 157, 177, 1963.
[5] Hiatt, H. H. *J. mol. Biol.*, 5, 217, 1962.
[6] Sporn, M. B. and Dingman, W. *Biochim. biophys. Acta*, 68, 389, 1963.
[7] Scherrer, K., Latham, H., and Darnell, J. E. *Proc. nat. Acad. Sci., Wash.*, 49, 240, 1963.
[8] Maggio, R., Siekevitz, P., and Palade, G. E. *J. Cell Biol.*, 18, 293, 1963.
[9] Crawley, J. C. W. and Harris, H. *Expl. Cell Res.* 31, 70, 1963.
[10] Oehlert, W., Schultze, B., and Maurer, W. *Beitr. path. Anat.*, 122, 289, 1960.
[11] Edström, J.-E. and Beermann, W. *J. Cell Biol.*, 14, 371, 1962.
[12] Petermann, M. L. and Pavlovec, A. *J. biol. Chem.*, 238, 318, 1963.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

[13] Montagnier, L. and Bellamy, A. D. *Biochim. biophys. Acta*, 80, 157, 1964.
[14] Yankofsky, S. A. and Spiegelman, S., *Proc. nat. Acad. Sci., Wash.*, 48, 1069, 1962.
[15] Brenner, S., Jacob, F., and Meselson, M. *Nature, Lond.*, 190, 576, 1961.
[16] Gros, F., Hiatt, H. H., Gilbert, W., Kurland, C. G., Risebrough, R. W., and Watson, J. D. *Ibid.*, 190, 581, 1961.
[17] Yankofsky, S. A. and Spiegelman, S. *Proc. nat. Acad. Sci., Wash.*, 49, 538, 1963.
[18] Reich, E., Acs, G., Mach, B., and Tatum, E. L. 'Informational Macromolecules', p. 317. Academic Press Inc., New York. 1963.
[19] Staehelin, T., Wettstein, F. O., Oura, H., and Noll, H. *Nature, Lond.*, 201, 264, 1964.
[20] Munro, A. J. and Korner, A. *Ibid.*, 201, 1194, 1964.
[21] Fenwick, M. L. *Virology*, 19, 241, 1963.
[22] Rake, A. V. and Graham, A. F. *Biophys. J.*, 4, 267, 1964.
[23] Bergstrand, A., Eliasson, N. A., Hammarsten, E., Norberg, B., Reichard, P., and von Ubisch, H. *Cold Spring Harbor Symp. Quant. Biol.*, 13, 22, 1948.
[24] Harris, H. *Progr. nucleic acid Res.*, 2, 19, 1963.
[25] Harris, H. and Watts, J. W. *Proc. roy. Soc., B*, 156, 109, 1962.
[26] Watts, J. W. and Harris, H. *Biochem. J.*, 72, 147, 1959.
[27] Scott, J. F., Taft, E. B., and Letourneau, N. W. *Biochim. biophys. Acta*, 61, 62, 1962.
[28] Scott, J. F., Kaltreider, H. B., Boeker, F. A., and Taft, E. B. *Fed. Proc.*, 23, 168, 1964.
[29] Harris, H. *Proc. roy. Soc., B*, 158, 79, 1963.
[30] *Idem. Nature, Lond.*, 202, 249, 1964.
[31] *Idem. Ibid.*, 201, 863, 1964.
[32] Reich, E., Franklin, R. M., Shatkin, A. J., and Tatum, E. L. *Proc. nat. Acad. Sci., Wash.*, 48, 1238, 1962.
[33] Prescott, D. M. *J. Biophys. Biochem. Cytol.*, 6, 203, 1959.
[34] *Idem. Expl. Cell Res.*, 19, 29, 1960.
[35] Cummins, J. E. and Plaut, W. *Biochim. biophys. Acta*, 80, 19, 1964.
[36] Schweiger, H. G. and Bremer, H. J. *Expl. Cell Res.*, 20, 617, 1960.
[37] Konrad, C. G. *J. Cell Biol.*, 19, 267, 1963.
[38] Harris, H. and LaCour, L. F. *Nature, Lond.*, 200, 227, 1963.

Book reviews

REFERENCE BOOKS

A Dictionary of Scientific Units, including Dimensionless Numbers and Scales, *by H. G. Jerrard and D. B. McNeill. Pp. 197. Chapman and Hall, London. 1963. 21s. net.*

The authors of this book present concise, up to date, and interesting information on the units and standards of measurement, with descriptions of the dimensionless numbers and scales. It includes the definitions and also adequate historical details of all the accepted units commonly used in science and technology. It also includes particulars of less widely known units in terms of which measurements in special fields are sometimes expressed and which often put difficulties of comprehension in the way of the general reader. Altogether there are some four hundred entries supplemented by about five hundred source references, the latter constituting a most valuable feature of the book. The five appendices comprise a table of values of fundamental physical constants; a brief description of the principal national and international authorities concerned with the definition and recommendation of measurement units; a table of United Kingdom and United States weights and measures; conversion tables for the various units of twenty-two quantities of measurement; and finally a table of conversion factors between MKS and cgs units.

The dictionary is attractively produced, contains very few misprints, and, despite one or two misapprehensions recognizable by the expert, is very accurate. It is recommended as a ready reference for students, teachers, and all those interested in scientific and technological measurements. *H. Barrell*

RELATIVITY

Gravitation and Relativity, *edited by Hong-Yee Chiu and William F. Hoffmann. Pp. xxxv+353. W. A. Benjamin Inc., New York and Amsterdam. 1964. $15.75.*

This useful book consists of the notes of a series of lectures presented at a seminar in New York in 1961 and 1962. The work gives an American view of general relativity, but a somewhat deficient one, because certain important American schools of thought are omitted. This view may be summed up in the ideas of experimental content of the theory, relation with the rest of physics, and the analysis of Mach's principle.

The most interesting chapter (because it contains the newest material) is that by Anderson on relativity principles. There has been for many years an argument in general relativity between Fock and a few of his followers on the one side, who believe that certain particular co-ordinate systems are physically required in relativity (the harmonic co-ordinates), and the other workers in the field, who believe with Einstein that all co-ordinate systems are equally valid, although of course some may be more convenient than others in particular problems. Anderson advances an anti-Fock argument, but it brings to bear, for the first time, arguments as powerful and profound as those of Fock.

To summarize, the book is largely a progress report on a subject which is still developing rapidly. Little is said about the problem of quantizing the theory or about the solutions of the theory corresponding to radiation. Within its self-imposed limits, however, it is an enlightening and valuable summary.

C. W. Kilmister

PROPERTIES OF MATTER

The Mechanical Properties of Matter, *by A. H. Cottrell. Pp. x+430. John Wiley & Sons, New York, London, and Sydney. 1964. 70s. net.*

This is an admirable account of the mechanical properties of matter, differing in two respects from the standard textbooks on what is known to physicists as properties of matter. These are, firstly, the omission of the usual elaborate treatment of the measurement of gravitational acceleration and of the Newtonian constant, which accords with the introduction of the word 'mechanical' in the title, and secondly, the masterly manner in which much modern work is introduced and explained. It is indicative of the way in which recent discoveries are considered that the frontispiece is from a photograph, demonstrating the atomic structure of tungsten, reproduced last year in an ENDEAVOUR article on field-ion microscopy, and that there is discussion of the abnormally strong fibres known as whiskers. The fracture of solids, a field in which much progress has been made of late, is authoritatively discussed in a special chapter.

As is to be expected in a book by Professor Cottrell, particular attention is given to crystal structure, the dislocations and other imperfections of which play so

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

important a part in the modern theory of the mechanical behaviour of metals. Polymers receive due attention. It must not be thought, however, that the standard properties of gases and liquids are neglected: the fundamentals are developed with great clarity. Altogether, this is a book in which both the classical aspects of the subject and modern developments are treated with particular distinction and lucidity. It is sure of a warm welcome by students, staff, and others concerned with the subject.

E. N. da C. Andrade

SURFACE SCIENCE

Surface Science, *edited by Harry C. Gatos. Vol. I, no. 1, January 1964. Pp. 124. North-Holland Publishing Co., Amsterdam. 1964. 116s. net for 500-page volume.*

It is fashionable, but irrational, to bemoan the appearance of yet another journal. In fact, there is much to be said for proliferation if it checks the growth in physical dimensions and technical range of existing journals and leads to readier access, greater homogeneity of material, and speedier publication of research—always provided, of course, that standards are maintained and the cost kept down.

The editor of this new journal maintains that there exists a distinct need for a publication to deal exclusively with fundamental theoretical and experimental studies in the physics and chemistry of surfaces. 'Surfaces' is to be read as interfaces, and such applications of surface science as catalysis, corrosion, and colloids (and presumably biological membranes) are to be excluded.

It remains to be seen whether researchers from different disciplines will be united by the journal into an international surface-science group. This first issue is distinctly one-sided; all the papers are concerned with the surfaces of solids, and most of them relate to the ubiquitous semiconductor. A surface chemist concerned, for example, with monolayers on water would not find much to interest him.

The standard of the papers is comparable with that to be expected of a journal of a learned society. The quality of production is excellent, but the price per page is very high—about five and a half times that of the *Transactions of the Faraday Society*, an economical journal that could have taken all of these papers.

J. A. Kitchener

CHEMICAL KINETICS

Chemical Kinetics of Gas Reactions, *by V. N. Kondrat'ev (translated from the Russian by J. M. Crabtree and S. N. Carruthers, edited by N. B. Slater). Pp. xiv+812. Pergamon Press, Oxford. 1964. £5 5s. net.*

Chemical kinetics has for several decades been one of the major branches of physical chemistry, of importance both in its own right as a study of molecular behaviour, and for its applications to problems of inorganic and organic chemistry. The Russians have made outstanding contributions to the field, and Professor Kondrat'ev himself is one of the leaders of the Russian school.

This book has the advantage of being written by an acknowledged authority, and of being detailed and comprehensive while at the same time offering a lucid and careful exposition of fundamentals. With some eight hundred pages, it is rather beyond the scope of undergraduate students, though these would find selective reading of various sections profitable. It will be of great value to the post-graduate student and the researcher, and is nearly comprehensive enough to count as a work of reference. In this connection it would benefit by a rather more elaborate subject index than that provided.

Naturally enough, those who have worked in the subject may find things to challenge here and there, but the treatment throughout is fair and objective, and the book is a valuable addition to the literature of general chemistry.

C. N. Hinshelwood

INFRA-RED SPECTROSCOPY

Chemical Applications of Infrared Spectroscopy, *by C. N. R. Rao. Pp. xiii+683. Academic Press, New York and London. 1964. 139s. 6d. net.*

In the author's words, this volume's aim is to present the basic concepts, measurements, and techniques of infra-red spectroscopy and to survey, as completely as possible, its chemical applications. After a fashion the aim is achieved. Basic concepts are described, in places at a dangerously superficial level, and are followed by sections on instrumentation and technique. Five chapters are concerned with characteristic group frequencies in organic compounds, and a further six cover a variety of topics, including inorganic compounds, specific applications in organic and biochemistry, high polymers, and quantitative analysis. Facts there are in plenty, so much so that one suspects a desperate desire on the author's part to get as much information in as possible, whatever the price. The price too often is a lack of any adequate discussion, and the style is that of a condensed review article. Some of the information, notably on near and far infra-red correlations, is welcome, but far too much of it is a straightforward repetition of data readily available in other texts. In an appendix on the teaching of infra-red spectroscopy, the author suggests that all the material in the book can be given in twenty-five one-hour lectures. It is a daunting challenge.

J. K. Brown

MASS SPECTROSCOPY

Interpretation of Mass Spectra of Organic Compounds, *by Herbert Budzikiewicz, Carl Djerassi, and Dudley H. Williams. Pp. xiii+271. Holden-Day Inc., San Francisco. 1964. $8.75.*

The discussion of mass spectra in this book is limited to spectra produced by collisions of electrons of about 70 eV energy with isolated molecules of the particular compound. Mechanistic schemes are proposed for the formation of the more abundant ions in numerous mass spectra; some of these may be to a certain extent speculative, but many of them are substantiated by isotopic labelling with deuterium. The authors also make use when possible of the results of high-resolution mass spectrometry. The interpretations proposed use standard organic chemical concepts, as they are called in the book, and are thus along lines familiar to the organic chemist. Much is gained by considering together the mass spectra of members of a class of related compounds.

This book should be of value to those planning to use mass spectrometry in organic chemical research. There is intentionally no discussion of instrumentation and other practical matters, and the authors aim to avoid overlapping other texts on mass spectrometry. The book therefore needs reading by the uninitiated organic chemist in conjunction with some other work.

A. J. B. Robertson

ORGANIC CHEMISTRY

Advances in Physical Organic Chemistry, *edited by V. Gold. Vol. II. Pp. xii+288. Academic Press, London and New York. 1964. 63s. net.*

This volume is somewhat smaller than the first in the series, and consists of four sections. The first deals with isotopes and organic reaction mechanisms. The isotope dilution method is described, and developed to include the more sophisticated methods involving multiple labelling and the combination of tracer and stereochemical studies. The effect of isotopic substitution on the chemical and physical properties of molecules is also

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

discussed. The next section deals with the use of volumes of activation for determining reaction mechanisms. This section gives an excellent account of the effect of pressure on reaction rates and shows how the volume of activation can be determined experimentally and how its numerical value can indicate the most likely rate-determining step of a complex reaction. Then follows a section on hydrogen isotope effects in aromatic substitution reactions. This is discussed in some detail, and it is shown how the effect may be used to decide between alternative reaction mechanisms. The last section deals with reactions of energetic tritium and carbon atoms with organic compounds. This is a useful account of the way in which high-energy atomic species can be produced. New types of reaction take place, and new concepts are required in order to understand them.

The sections in this book can be read with advantage by non-specialists in these fields and are well provided with references for the benefit of the reader who wishes to seek further details. The volume maintains the high standard of its predecessor and can be recommended to chemists who wish to gain further information about these important fields of study. *James C. Robb*

Physical Methods in Organic Chemistry, *edited by J. C. P. Schwarz. Pp. xi+350. Oliver and Boyd Ltd, Edinburgh and London. 1964. 50s. net.*

Preparative chemistry, whether inorganic or organic, has become dependent upon physical techniques for the determination of electronic and molecular structures, and the present book is intended to provide an introduction to physical methods for organic chemists, primarily at the undergraduate and the immediate post-graduate level. The first four chapters are concerned with electronic and, more particularly, vibrational spectroscopy, covering such topics as instrumentation, characteristic group vibrational frequencies, the absorption wavelengths and intensities of the common chromophores, and analytical applications. The following two chapters cover the techniques of magnetic-resonance spectroscopy and optical rotatory power measurements, and their application to structural studies. The use of mass spectrometry and X-ray diffraction methods in structure analysis and the determination of molecular weights and dipole moments are discussed in the remaining four chapters. In general, the authors adopt an empirical approach to the use of physical methods for the determination of molecular structure, but sufficient theory, and excellent sets of references, are given to stimulate the enquiring student. The themes of the various chapters are illustrated by well-chosen examples of current interest and by informative tables and diagrams. Organic chemists will find this book a useful one, supplementing other works available in the same field. *S. F. Mason*

PORPHYRINS

Porphyrins and Metalloporphyrins, *Vol. II, by J. E. Falk. Pp. xiii+266. Elsevier Publishing Co. Ltd, Amsterdam. 1964. 75s. net.*

Metal chelates of porphyrins and the closely related chlorins are among the biologically most important natural products, being involved in transfer of oxygen and electrons and in photosynthesis. In recent years Australia has been very strongly represented in this broad field of research; this new book by one of the leading Australian chemists is therefore welcome. Its scope is clearly defined by the sub-title—their general, physical, and co-ordination chemistry, and laboratory methods. There is little mention of synthetic organic chemistry, and thus the book complements the classical 'Fischer-Orth'. Like 'Fischer-Orth', Dr Falk's book will be an indispensable practical manual, because it contains a wealth of physical data and laboratory know-how in a relatively small space. The value of proton magnetic resonance seems to be underestimated, and although there are few publications on thin-layer chromatography of porphyrins, it is surprising not to find any mention of this technique. The exposition is clear, but the treatment is probably too specialized for general readers. The book is strongly recommended to all workers in the porphyrin field. *G. W. Kenner*

CRYSTAL DEFECTS

Point Defects in Metals, *by A. C. Damask and G. J. Dienes. Pp. xiii+314. Gordon and Breach Inc., New York and London. 1964. $19.50.*

Imperfections in crystals are fascinating things. They determine some of the most important properties of matter; and the very regularity of the crystal structure forces them into precise forms, so that they exist as a kind of well-defined elementary particle inside a crystal. This book deals with the vacancy and the interstitial, two point-defects created in a metal crystal by a missing or an extra atom respectively. The vacancy is particularly important, being mainly responsible for diffusion and chemical reactions in the solid state, various creep effects, and numerous effects involving dislocations. Interstitials are important mainly in radiation damage, where they are formed, with vacancies, by pair-creation.

Vacancies and interstitials are the simplest defects in metals, but nevertheless provide endless problems for scientific investigation of their atomic and electronic structures, energies of formation and movement, the various clusters which they form, and all their interactions with one another and with other defects and foreign atoms. The authors have given an admirably clear account of these topics, and their book will be most valuable for those starting work in the field and enjoyable for the mere visitor. They have confined themselves mainly to the basic physics of the subject, so that some of the striking recent developments in physical metallurgy concerning the parts played by vacancies in alloy precipitation and grain boundary processes are not discussed. This is perhaps inevitable when the purpose has been to present the central theory as clearly and completely as possible. *A. H. Cottrell*

GEOMORPHOLOGY

Fluvial Processes in Geomorphology, *by Luna B. Leopold, M. Gordon Wolman, and John P. Miller. Pp. xiii+522. W. H. Freeman & Co., San Francisco and London. 1964. 57s. net.*

There are many textbooks that deal with landforms, but few that deal in any detail with the processes that are assumed to have produced such landforms. A textbook concentrating on the study of geomorphic processes is therefore welcome. In this volume, the processes studied are especially those concerned with rivers, and to a lesser extent those concerned with hill-slopes. These two sets of processes, intimately interconnected on the Earth's surface, are central to geomorphology, for they have controlled the formation of most landforms. The emphasis on rivers partly reflects the interests of the authors and the problems on which they have worked; it also highlights the real shortage of quantitative data concerning hill-slopes.

Within the last two decades, progress in geomorphology has been made by applying statistical and other techniques to describe landforms more precisely, and by applying physical and chemical principles to field and laboratory studies. In both these directions, American geomorphologists have made outstanding

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

contributions. This book records this progress and indicates the bearing of the new quantitative data on classical geomorphic theories. A bold attempt is made to present and use the fundamentals of hydraulics to describe and explain river action. There are useful discussions on such topics as the value of theoretical or mathematical models in geomorphology, and on the relations between climate and denudational processes. In the section on landform development, there are brief useful descriptions and discussions of various methods used in dating the past.

This is an extremely valuable textbook for the advanced student and teacher in geomorphology in the universities.

V. B. Proudfoot

BACTERIAL GENETICS

The Genetics of Bacteria and their Viruses; Studies in Basic Genetics and Molecular Biology, *by William Hayes. Pp. xii+740. Blackwell Scientific Publications Ltd, Oxford. 1964. 84s. net.*

As the author states, this is a rather advanced textbook on the genetics of bacteria and bacteriophages for post-graduate workers in related fields. It will serve this purpose admirably, for it provides a masterly summary of the rapidly developing and highly significant field of modern molecular genetics of micro-organisms, and also reviews briefly but clearly the essential background material in classical genetics. Within a dozen years, enormous progress has been made in understanding the role of the nucleic acids in specifying how organisms develop and function. We know a great deal about the detailed structure of deoxyribonucleic acid, the manner in which it replicates, how it directs synthesis of proteins through the intermediary of ribonucleic acid, the nature of mutational change, and some of the amazing ways in which it is transmitted from one generation to another. DNA and RNA appear to serve as remarkably simple molecular codes.

We are also now beginning to understand some of the means by which the chemical reactions of living systems are regulated and integrated by feedback mechanisms that determine whether or not DNA specifications are made use of in protein synthesis, or that specify whether or not enzymes already present will function. This is a beginning towards understanding the puzzling problem of cellular differentiation in multicellular organisms.

William Hayes will be thanked by innumerable students and research workers whom he has spared the increasingly difficult task of reviewing and evaluating the original literature in microbial and molecular genetics.

George W. Beadle

RADIATION TECHNIQUES

Radiation, Radioactivity, and Insects, *by R. D. O'Brien and L. S. Wolfe. Pp. xv+211. Academic Press, London and New York. 1964. Cloth bound, 48s. net; paperback, 28s. net.*

This book, one of a series produced on behalf of the U.S. Atomic Energy Commission, is intended for the entomologist who wishes to learn about the use of radiation techniques and for the experienced user of such techniques who wishes to apply his methods to the study of insects.

The genetic effects of radiations will form the subject of another monograph; apart from that, the field is well covered. The effects of ionizing radiations are described. The apparent high degree of tolerance in insects results from the absence of cell division for long periods; delayed burns appear when mitosis is resumed. The methods and results of marking, or 'tagging', insects with radioactive substances for studies of their movements are covered. Radiosterilization may take the form of direct effects on both sexes by large doses of radiation or specific effects on the males, which are then liberated in sufficient numbers to swamp the normal males—as in the eradication of the screw-worm fly in Florida. The use of radioisotopes in the study of insect physiology and biochemistry, and the investigation of insecticidal action, is described; and, rather surprisingly, a chapter is included on the diverse effects of light in the physiology of insects.

V. B. Wigglesworth

MARINE BIOLOGY

Marine Bio-Acoustics, *edited by William N. Tavolga. Pp. xii+413. Pergamon Press, Oxford. 1964. £5 net.*

This book is a collection of papers presented at a symposium held in the Lerner Marine Laboratory, Bimini, Bahamas, in April 1963, which has been the centre of much of the pioneering work on animal-produced sounds in the sea. The first part of the book describes the facilities which have been set up there by the American Museum of Natural History; the complexity of the underwater hydrophone arrays and television cameras which are described illustrates the instrumentation developments that have really opened up this subject. Typical records of underwater sounds made at Bimini show a wide variety of biologically produced noises: some can be ascribed to an identifiable source, but the origin of many others is still obscure.

Both the physical and acoustical aspects of sound production and propagation are examined, and several papers deal with sound production by a wide variety of animals, from invertebrates to fish. Attention is drawn to the probable importance of air bladders in fish as resonators. The ability to detect sounds is also examined.

The final part of the book deals with cetacean sounds and provides convincing evidence of the efficiency of the echo-location mechanism of whales. Polar diagrams of the sound emission of dolphins show a directivity almost comparable to that of echo sounders.

The rapid advance of marine bioacoustics in the last decade owes much to the acoustical instrumentation resulting from defence research programmes: one must credit the United States Office of Naval Research for promoting the use of these developments in the field of pure science. Pergamon Press have produced an elegant volume depicting intriguing problems in a new field. It should be of interest to a wide range of scientists in adjacent disciplines.

Ronald Currie

CARCINOGENESIS

Mechanisms of Carcinogenesis: Chemical, Physical and Viral, *edited by E. Boyland.* British Medical Bulletin, *Vol. 20, No. 2. Pp. 87–164. The British Council, London. 1964. £3 10s. net per vol. of 3 numbers.*

This is the third issue of this bulletin devoted to carcinogenesis, and, as pointed out in the introduction, the timing of these numbers of the Bulletin is a clear index of the increasing scale and tempo of research. Thirteen topics are chosen for reviewing, as compared with twenty-one in 1958; yet the present issue, while more restricted in its title, is actually more comprehensive in scope. Much has been gained in perspective by the inclusion of a stimulating review on the relationships between cells and viruses and a useful summary of the recent findings bearing on the aetiology of Central African Lymphomata, and by the elimination of topics that have not advanced significantly of late.

The advances made since 1958 in the fields of alkylating agents, lactones and related substances, nitroso compounds, metallic substances, and natural products in relation to carcinogenesis, and of immunological aspects of carcinogenic action, are well covered. The

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

slowly accumulating knowledge about cocarcinogenesis is once again brought up to date; polycyclic hydrocarbons are discussed mainly from the viewpoint of their metabolism, in keeping with the general emphasis on mechanism of action. The review on radiation carcinogenesis is, disappointingly, restricted almost exclusively to human studies. Also included is a review of marginal interest, on the effects of alkylating agents on fertility.

I. Berenblum

BODY FLUIDS

Animal Body Fluids and their Regulation, *by A. P. M. Lockwood. Pp. vii+177. Heinemann Educational Books Ltd, London. 1963. 17s. 6d. net.*

In this book Dr Lockwood has summarized a great deal of information, much recently obtained, on the maintenance of salt and water balance in animals. The concentration and composition of blood and of the interstitial fluid around cells depends often on the animal's environment. Here are discussed examples from all the major animal groups from many habitats. The aquatic animals include marine invertebrates such as starfishes and worms, with permeable skins and body fluids similar to sea water; freshwater animals like the mussel *Anodonta* and the fishes, baling out with their excretory organs water which enters their bodies osmotically, and taking up such ions as chloride from the almost salt-free medium to replace those lost by diffusion; and marine turtles and sea-birds, no longer permeable to salt and water except through the gut, getting rid of excess salts from their food as salt tears by means of special glands in the head.

Also explained is the physiological basis of the legendary powers of the camel in its desert treks, and the ability of desert rats to live with a water supply that is chiefly self-produced metabolic water from the utilization of their food, conserved by their most efficient kidneys.

Helpful diagrams are a feature of the book, which covers its subject at a level suitable for university students.

J. D. Robertson

MOLLUSCS

Physiology of Mollusca, *Vol. I, edited by Karl M. Wilbur and C. M. Yonge. Pp. xiii+473. Academic Press, New York and London. 1964. 114s. 6d. net.*

This book is an important and welcome addition to comparable volumes on crustaceans, fish, and birds, and it fills a very obvious gap. It is scheduled to appear in two volumes and should prove invaluable to all who study molluscs. Volume I is written by a distinguished list of contributors and is both authoritative and informative. There is an introductory chapter on classification and structure by Morton and Yonge, primarily concerned with the evolutionary interpretation of studies of functional morphology. Then follow chapters on ecology, reproduction, and development; culture of bivalve larvae; growth; shell formation; osmoregulation; neuromuscular physiology; locomotion; buoyancy; and special effectors (for example luminescence and pigments). This list of contents reveals that the editors have interpreted the word physiology widely, and half this volume would not be regarded as strictly physiological by some workers. Such a treatment is not necessarily to be scorned; for example, I found the two chapters on physiological ecology most interesting, and they should prove helpful summaries to ecologists and physiologists alike. However, in places this approach seems unfortunate; the chapter on reproduction is mainly concerned with gametes and oviposition and little is said of the physiology of reproductive systems.

C. J. Duncan

HISTORY OF SCIENCE

William Herschel and the Construction of the Heavens, *by M. A. Hoskin, with* Astrophysical Notes *by D. W. Dewhirst. Pp. 199. Oldbourne Book Co., London. 1963. 35s. net.*

Dr Hoskin's book is concerned with Herschel's work on stellar astronomy and only mentions in passing his life, his construction of the giant telescopes, and his work in radiation and optics. The author has chosen to let Herschel himself tell most of the story by reprinting the important parts from eight of Herschel's own papers on double stars, the motion of the solar system through space, the structure of the Milky Way and other galaxies, and the evaluation of stellar magnitudes and distances. These papers, together with Dr Hoskin's generally very penetrating comments, provide the material for a very interesting case study of science in the making, and it is to be hoped that the book will serve as a model for similar works in other fields. As Dreyer's 1912 edition of Herschel's papers has been out of print for many years, the present work is most welcome. It is to be criticized only on one ground—the absence of an index, which should never be missing from a work of this kind.

O. Pedersen

Experiments and Considerations touching Colours, *by Robert Boyle. Edited by Marie Boas Hall. Pp. lxvi+423. Johnson Reprint Corporation, New York and London. 1964. $12.50.*

In her excellent introduction to this reprint, the learned editress says that the book deserves to be far more widely known than it now is, but also refers to the 'gentlemanly ornateness, particularly apparent in his early works' of the style. The original publisher, in his words to the reader, states that the book deals with 'one of the Abstrusest as well as the Gentilest Subjects of Natural Philosophy'. Boyle was a gentleman, which neither Newton nor Hooke could claim to be, and wrote at great and florid length, with many polite divagations and parenthetical disquisitions, so well travestied in Swift's 'A Meditation upon a Broom-Stick'. This means that, by its prolixity, the book is not particularly easy to read in this precipitate age.

As regards the physics of colour, the book contains many acute observations, especially about the colours of thin films, and shows an understanding of the nature of the colours white and black, connecting black with an absorption of light which leads to warming. A long and typical disquisition about the complexion of negroes has little to do with the scientific notions of colour. There is little about the properties of light: no approach to Newton's perception of the relation of light and colour.

The book is, in fact, more important for its contributions to chemistry than to physics. Pepys recorded 'finishing Mr Boyle's book of colours, which is so chymical, that I can understand but little of it. . . .' It deals at length, and in a pioneering way, with chemical indicators, in particular syrup of violets, which all acids turned red and all alkalis blue. Needless to say, the matter is helpfully treated in the introduction by Dr Boas Hall, known for, among other works, her 'Robert Boyle and Seventeenth-century Chemistry'.

It should be added that the book is an exact reproduction of the edition of 1664, including the frontispiece in red and black, the coloured text somewhat misplaced, as in the original.

E. N. da C. Andrade

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by [illegible]

ENDEAVOUR

VOLUME XXIV MAY 1965

A review of the progress of science, published in five languages

Editor TREVOR I. WILLIAMS, M.A., B.Sc., D.Phil., F.R.I.C.
Foreign Editor G. N. J. BECK, B.Sc., A.M.I.E.E.
Assistant Editor W. A. OSMAN, B.Sc., M.Sc., A.R.C.S.

Contents

378.3:53/59
62 Editorial: Educating the young scientist

548.55:546.26–1:622.336
63 The anisotropy of graphite
A. R. Ubbelohde, C.B.E., M.A., D.Sc., F.R.S.

541.128.13
69 Heterogeneous catalysis
D. A. Dowden, B.Sc.

581.145.1
74 The initiation of flowering
Frank B. Salisbury, B.Sc., M.A., Ph.D.

547.567
81 Quinones as biological catalysts
R. A. Morton, Ph.D., D.Sc., F.R.I.C., F.R.S.

523.4
87 The planets
A. Dollfus, Docteur ès Sciences

591.9 (26.01)
95 The surface fauna of the ocean
P. M. David, M.A.

622.765:622.366
101 Development of the theory of the flotation of sulphide ores
M. G. Fleming, Ph.D., and J. A. Kitchener, D.Sc.

621.385.63
106 The development of the travelling wave tube
R. Kompfner, Dipl. Ing., D.Phil.

111 Book reviews

Some books received (cover iii)

Communications should be addressed to the Editor, Endeavour, South Block, Thames House, Millbank, London S.W.1 Telephone: Tate Gallery 2181

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Educating the young scientist

The further the frontiers of knowledge are advanced, the longer the journey young scientists must make before they themselves can contribute to progress. The importance of a sound and early start to scientific education needs no emphasis, and in Britain a very important contribution is now being made by the Nuffield Foundation, an independent charitable organization. During the last three years, this has been engaged in a thorough revision of science curricula and teaching methods for schools. A number of its recommendations are already being put to the test of practical experience in representative schools throughout Britain, and the results are encouraging.[1] In taking account of the needs of those who will go on to a university and ultimately follow a career in science, sight has not been lost of the fact that these represent a small minority of the population. It is recognized equally that today science must form part of any system of liberal education, and that the period of secondary education is of particular importance.

Although the present emphasis is on teaching the 11–16 year age group, it is clear that the project will have considerable repercussions on scientific education generally, for this is a continuous process. At the upper end of the scale, consideration is being given to the needs of the 16–18 year age group, and this in turn inevitably leads on to the question of university science teaching. Similarly, at the lower end of the scale attention is being given to the possibility of introducing some science into primary school teaching.

Naturally, this project is directed in the first instance to the improvement of science teaching in Britain. Nevertheless, it reflects a world-wide interest in scientific curricula and teaching methods, and the general principles involved are of wide interest. The Foundation is therefore already considering how it may encourage appropriate overseas organizations to launch projects of their own, designed to take account of local conditions.

While accepting that some drastic reform in science teaching is generally needed, the sponsors are by no means dogmatic in their recommendations. Very properly, their intention is not to replace one rather rigid system by another; rather, they want to set in train a continuing change in British scientific education. That change is necessary is scarcely surprising, for the present system was conceived not only before many major developments in science with which the student must now be familiar, but in an economic, social, and political climate quite different from that of today. To urge the need for reform is no more than to say that times change and we must change with them.

The Nuffield project covers the whole field of chemistry, physics, and biology with commendable thoroughness. It considers not only what should be taught but how the imagination of the student can best be stimulated. In concluding that the best route is by experiment and practical inquiry—in line with revision of teaching methods in science adopted in recent years in the United States—the project at once became involved in the design of new items of apparatus, and the modification of many existing ones. In consequence, arrangements had to be made with manufacturers to ensure that these are available in sufficient quantities and at a reasonable price. So far as the latter is concerned, the approach has been realistic; the sponsors are fully aware that it is useless to advocate changes involving impossibly high expenditure.

The role of teaching aids, notably films, has been examined in detail, and a large number of 8 mm film loops, for use with simple back projectors, have been produced. After consultation with the Publishers' Association, a considerable book-publishing programme has been put in hand. In preparation for very extensive trials during the school year beginning in September 1966, some 100 titles are being put into production; the first printing will be close on 3 million books. These include teachers' guides, books for use in class, reference books, and laboratory notes.

It is accepted that the final test of the benefit of the new courses to students must be by examination, and very careful thought has been given to the preparation of new papers. It has been necessary not only to see that these fairly reflect the new curricula, but to safeguard the interests of students who—at least during a period of transition—will be taking examinations very different from those set for their contemporaries still following the present programme.

The success of a radically revised teaching programme must depend on the teachers themselves having a proper understanding of the principles involved, and to ensure this, they must be given an opportunity to study the new methods in detail. Last summer, a start was made with this at a two-week conference for some 300 teachers, organized in collaboration with the Department of Education and Science. This made clear that an intensive one-week course, although not ideal, would do much to help a teacher to introduce a class to new material and methods.

To commit a nation to a radical reform of its scientific educational system is, of course, a major responsibility. Before embarking on it, it is essential to know not only that the principles are sound and acceptable, but that as far as possible practical difficulties will be eliminated before full-scale operation is attempted. To ensure this, preliminary trials are essential. The Foundation in fact began these as early as 1962, but a more ambitious test programme is at present under way. In this, 49 schools are co-operating in physics, 56 in chemistry, and 66 in biology; in all, nearly five hundred separate classes are involved. These extensive trials are the prelude to the adoption of the new programme by a substantial proportion of schools in Britain from 1966 onwards.

Such a considerable and complex programme, involving close co-operation with many government and private organizations, is necessarily expensive, though the sum involved is relatively small considering the vital importance of the subject. The brunt of the expenditure has been borne by the Nuffield Foundation. In 1961, £250,000 was set aside for the project, and a further £180,000 has since been given. In addition, a further £250,000 has been required to finance the publication programme, though it is expected that this will in due course be recovered as revenue from sales; a total expenditure of £1m has been approved. Although it is too early to assess the full consequences of the project, it is already clear that the Foundation is making a considerable contribution to scientific education.

[1] The Nuffield Foundation Science Teaching Project: Progress Report (October 1964).

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

The anisotropy of graphite

Digitized by Arya Samaj Foundation Chennai and eGangotri

A. R. Ubbelohde

Single crystals of graphite are markedly anisotropic, but it has become possible recently to make such crystals large enough for their properties to be examined. This article describes the preparation and properties of what are effectively large single crystals of graphite. It also suggests some uses for the anisotropic material, including a thermocouple made throughout of one substance.

Graphitic carbon is a very valuable material for electrodes, as used in extraction metallurgy, and in the form of carbon brushes. Its high melting point and chemical inertness account for a further range of uses as a high-temperature refractory, and its properties as a neutron moderator have led to extensive applications of graphite in the atomic power industry.

However, all the conventional and well-established uses for graphite employ polycrystalline material. Single crystals of graphite are anisotropic, that is, they have strikingly different properties in different directions. Graphite technologists have hitherto as it were thrown away this characteristic, by manufacturing polycrystalline material with a built-in compensation of crystalline properties. However, deliberate use of the anisotropy of graphite could lead to important new applications. Some of these are outlined in what follows.

Rapid advances are now taking place in basic research on solids. The exceptional anisotropy of graphite, which for many properties is more pronounced than in most other crystals, makes this substance of particular interest for physical theories of the solid state. There is an increasing number of ways in which the anisotropy can be investigated experimentally, and the results are stimulating new theoretical advances in physical science.

Some physical aspects of crystal anisotropy

Crystallographers have long known that certain classes of solids show different properties in different directions. For example, the double refraction shown by calcite can easily be seen in the large transparent crystals found in nature, and is a manifestation of anisotropy in the refractive index. Quite generally, geometrical theories of crystal symmetry show that crystal properties must, in many cases, be unequal in different directions.

The ratio of numerical values of any property of a crystal in the directions of its principal axes (the anisotropy ratio) is unity for cubic crystals. For crystals of lower symmetry, the anisotropy ratio will depart from unity, but often only to a small extent. This can usually be explained when the dependence of crystal properties on crystal forces is taken into account. Advances in this branch of crystal physics have, however, been seriously hampered by the fact that only very few characteristics of a crystal can be conveniently measured on the small specimens normally found in nature. New ways of growing large crystals have become necessary as technological applications of anisotropy have become important.

Geological deposits of graphite often contain material with a markedly preferred orientation of its crystallites. However, natural crystals of graphite of any size that are near ideal are probably considerably rarer than diamonds, and even the fairly perfect but small crystals found in certain limestone deposits (such as at Ticonderoga, United States) tend to be spoiled by inclusions of inorganic impurities. Interest in the anisotropy of graphite has been greatly stimulated by the development of technical methods for synthesising large pieces with well-oriented crystallites. The present article is particularly concerned with the progress of these synthetic methods, and with the anisotropy of the crystal properties, which is much more easily studied on large specimens.

Structure of graphite in relation to the synthesis of well-oriented material

In order to follow this progress, three principal features need to be kept in mind about the structure of graphite.

1. *The carbon hexagon networks.* Many leading features of the crystal structure of graphite are well known (figure 1). In a perfect crystal, the carbon atoms are bonded together into planar hexagon networks. The C—C bond distance between carbon atoms in any such network is 1·415 Å. This is practically the same as in benzene. In the language of mathematical chemistry, this distance corresponds to a bond order of 3/2, intermediate between single and double bonds. Thus, each planar network in a graphite crystal may be regarded as a giant aromatic molecule, and hence as a member of a homologous series of aromatic hydrocarbons with planar fused rings extending in two directions. This particular viewpoint throws light on the anisotropy of chemical properties of graphite. At its edge, each network may satisfy carbon valencies, which otherwise would remain free, by

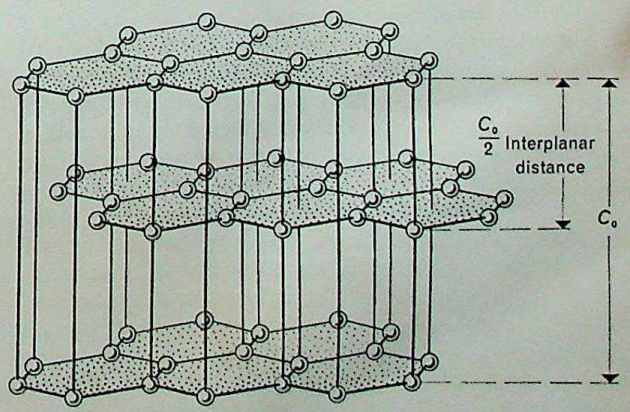


Figure 1 Crystal structure of graphite.

A. R. Ubbelohde, *C.B.E., M.A., D.Sc., F.R.S.*
Was born in 1907 and educated at St Paul's School, London, Christ Church, Oxford, and the University of Göttingen. He was a Dewar Fellow of the Royal Institution from 1935 to 1940, and he worked on explosives for the Ministry of Supply from 1940 to 1945. From 1945 to 1957 he was Professor of Chemistry at Queen's University, Belfast, and since 1957 he has been Professor of Thermodynamics at Imperial College, London; he is also the Head of the Department of Chemical Engineering and Chemical Technology. His research interests are in thermodynamics and chemical physics, particularly of solids and melts, and in graphite and its crystalline components.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

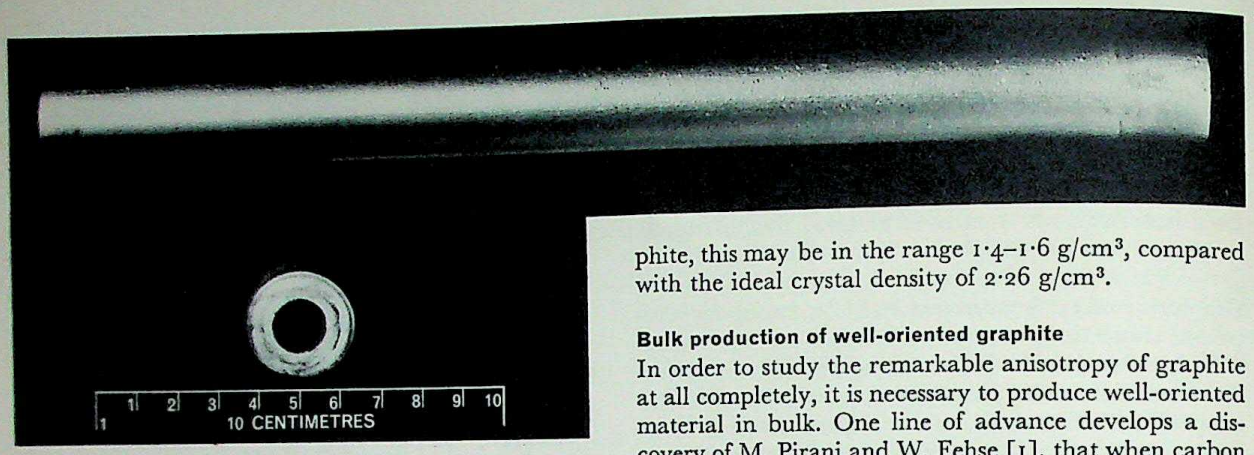


Figure 2 Thick tube of pyrolytic graphite.

combination with atoms other than carbon to form groups such as ≡CH, −CHO, and =C=O. When graphite reacts chemically, for example when it is oxidized, attack begins most readily at these network edges, except at the highest temperatures. To some extent, edge groups modify various properties of the layers and influence the anisotropy. However, by making measurements on a series of graphites with varying degrees of defects, extrapolated values for 'ideal' graphite can usually be calculated with some confidence. Networks can also show internal defects, such as missing atoms. These need not be discussed further here.

2. *The stacking of the networks.* Figure 1 also shows that, in the ideal graphite structure, the networks are accurately stacked over one another in a staggered (hexagonal) sequence *ababab*. Physicists have not yet completely accounted for the forces that control orderly stacking of these networks, in view of the facts that the minimum distance between the layers is never less than 3·35 Å, and that such large separations in crystals seldom result in more than weak forces of interaction. Indeed, this weak interaction is thought to explain why graphite can act as a lubricant, allowing its layers to slip past one another easily when shearing forces are applied to the crystals. Further evidence for weak interaction is the fact that alternative stacking arrangements can be introduced in graphite, such as rhombohedral, with sequence *abc*, *abc*, *abc*, or turbostratic, with layers parallel but without any other ordering of the networks. Nevertheless, both these alternatives prove to be less stable than the hexagonal. They revert to it when graphite is annealed at very high temperatures.

3. *Conglomerate packing of crystallites in the polycrystalline solid.* In commercial polycrystalline graphite, individual crystallites are more or less well ordered but with varying amounts of the defects referred to in 1 and 2. Neighbouring crystallites are agglomerated, and their axes assume practically any orientation relative to one another. Whatever the orientations, variations of bonding between atoms at the edges of neighbouring crystallites appear to establish fairly stable crystal boundaries. However, orientations and boundaries in the conglomerate differ from the much better known ones in many metals, in that polycrystalline graphite normally incorporates a considerable volume fraction of clefts and pores. Some idea of the pore volume may be obtained from the density. For conventional Acheson process graphite, this may be in the range 1·4–1·6 g/cm^3, compared with the ideal crystal density of 2·26 g/cm^3.

Bulk production of well-oriented graphite

In order to study the remarkable anisotropy of graphite at all completely, it is necessary to produce well-oriented material in bulk. One line of advance develops a discovery of M. Pirani and W. Fehse [1], that when carbon compounds were cracked on to thin carbon filaments heated to about 2000°C, deposits of pyrolytic graphite were formed; in these the crystallites have their *c*-axes predominantly normal to the heated surface. Various technological developments of this discovery are currently used in the production of fairly large pieces of pyrolytic graphite. By supplying larger heating currents, larger formers can be used in what is essentially a similar procedure [2]. For example, the tube of well-oriented graphite illustrated in figure 2 was produced in our laboratories by cracking methane on to a cylindrical carbon former, the surface of which was maintained at 2180°C by a current of about 2500 amperes. Deposition of even thin layers requires several hours to form a well-ordered deposit. When more rapid formation of well-oriented graphite is needed, so as to produce pyrolytic graphite commercially, this may be deposited in furnaces heated to uniform temperature. Induction heating has also been used in special cases when electrodes of any kind had to be avoided [3].

Pyrolytic graphite produced on cracking hydrocarbons by any of these means is still some way from approximating to perfect parallelism of the crystallites. Figure 3 shows a photomicrograph of the section of a typical deposit on a plane heated surface. Crystallite arrangements originate from mechanisms of nucleation and growth of the carbon produced by cracking hydrocarbons, which lead to the cone growth illustrated. Even with surfaces whose shape is far from planar, the approximate normality of cone axes to the surface in the deposits persists, and can be important for such technological applications as rocket nozzles.

When pyrolysis is carried out on to formers heated by electric currents, quite a steep temperature gradient is set up in the hydrocarbon gas flowing past the former. The product of this process, as compared to that of furnaces heated to uniform temperatures, has the advantage that rival processes of carbon formation in the gas phase, leading to soot particles in this phase, are kept to a minimum. This is because any soot tends to become incorporated in the deposits of pyrolytic graphite. However, a disadvantage of heated formers is that a gradient of temperature is also set up in the deposited layers because the thermal conductivity perpendicular to the basal planes of the crystallites is low. With deposits of pyrolytic graphite thicker than a millimetre or two, if the outermost layers are maintained at the optimum (about 2150°C) for cracking, the innermost layers may then exceed annealing thresholds (about 2700°C). This can

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

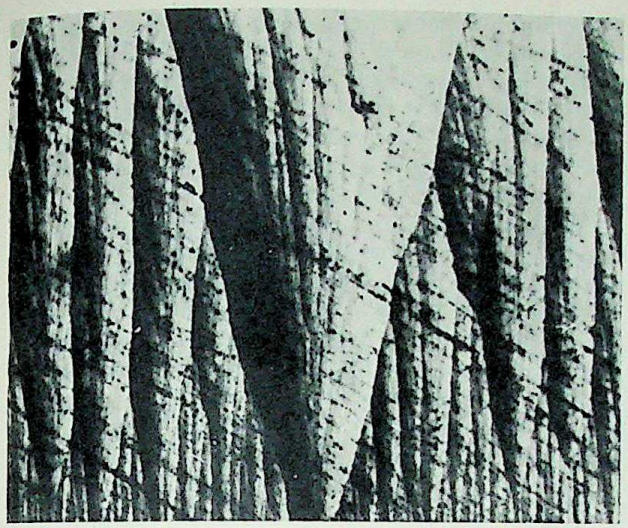


Figure 3 Photomicrograph of section of deposit of pyrolytic graphite, normal to the substrate. (×500)

give marked non-uniformity of properties normal to the depositing surface.

Whichever method of production is used, the orientation of crystallites in pyrolytic graphite is still far from ideal. Figure 4a records this fact in the form of the angular distribution of crystallite axes about a mean direction normal to the surface of deposition.

To produce large pieces of near-ideal graphite, it is necessary to eliminate the more highly disordered crystallites and intercrystallite carbon from well-oriented material, such as pyrolytic graphite. A classic procedure for making large single crystals of metals from polycrystalline specimens employs annealing following stress. This cannot be applied without modification to graphite, because the necessary annealing temperatures are so high that there are extensive vaporization losses. By way of illustration, when pieces of pyrolytic graphite were heated in vacuo to about 3500°C, the residual solid showed a bulk density of only about 1·6 g/cm³. It contained numerous voids and cracks, though the orientation of crystallite axes in the material that remained was much closer to ideal single crystals (figure 4, curve 2).

To meet this difficulty, a shearing stress must be maintained on the graphite while it is above 3000°C. One quite successful technique for doing this involves a temperature gradient in thick layers of pyrolytic graphite, as deposited on to an electrically heated former. By suddenly raising the temperature of this heated former, the inner layers can be brought to 3000°C, or even higher, while they remain subject to stress from the outermost layers of the deposit, whose temperature need not exceed about 2000°C. Extremely well oriented graphite with theoretical crystal density is produced in this way, but only in rather thin layers. This material is still not very suitable for studying anisotropy, since it is not very thick in the direction of the *c*-axis (figure 4, curve 3 [4, 5]).

A method with much more general possibilities produces thick pieces of near ideal graphite by applying axial pressure on cylinders of well-oriented graphite while these are heated to around 3000°C. The cylinders are contained in an envelope of commercial polycrystalline graphite, which is sufficiently plastic at these operating temperatures to expand radially. A radial movement of about 12–15 per cent removes practically all the misorientation of crystallites in the pyrolytic graphite used as starting material (figure 4, curve 4). Final annealing of the products at about 3200°C under light pressure yields compact cylindrical specimens up to 2 cm thick, well suited for the determination of anisotropy ratios. For many purposes these cylinders approximate to large single crystals of graphite, though geometrically they are still not quite perfect. The alignment of *c*-axes is practically ideal. Normal to this direction, the 'parallelized' crystallites have dimensions up to 5 μ or more. Because of the hexagonal symmetry, in the direction of the *a*-axis, boundaries between parallelized crystallites do not introduce any large strain energies, and as a consequence they are difficult to remove by annealing even at 3300°C. Fortunately, their presence is unimportant in evaluating many crystal properties. Scattering effects in transport properties, due to their presence, can usually be allowed for by calculation.

Anisotropy ratios of graphite

With the large pieces of near ideal graphite that are now available, it has been possible to verify and to complement earlier information, derived from studies on small natural single crystals, about the anisotropy. A brief review of anisotropy ratios (*a*-axis/*c*-axis) for which values or estimates can now be obtained is given below, followed by some technological applications.

Hardness. This technologically important quantity is difficult to measure in any well-defined way because of the various types of structural disorder possible in graphite. Across the planes of carbon atoms, resistance to cutting indicates hardnesses of about 9 moh. Ideal graphite may be even harder than diamond in this direction because of the bond order 3/2 between carbon

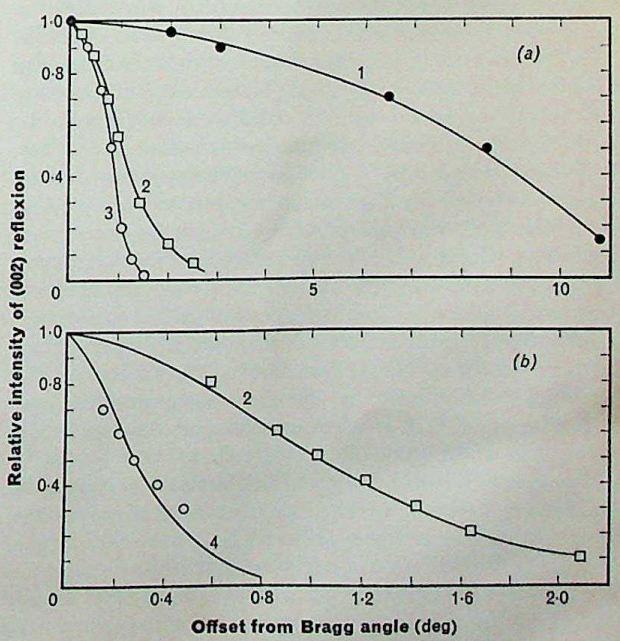


Figure 4 Angular distribution of *c*-axes of crystallites as a function of angle of deviation from the nominal axis of the specimen. Curve 1, pyrolytic graphite, deposited at 2180°C, annealed at 3000°C. Curve 2, same, but recrystallized at 3500°C without constraint (see text). Curve 3, graphite, stress-annealed *in situ*. Curve 4, graphite, stress-recrystallized by hot pressing.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

atoms in the networks. One way of using this property lies in producing graphite as whiskers or other shapes such that slip, which would release cutting forces, can be prevented. Parallel to the planes of carbon atoms, the theoretical hardness of ideal crystals is of course extremely low. It is easy to separate the carbon hexagon networks in near-ideal crystals, and anisotropy ratios of hardness may be as low as 1/100 or even 1/1000.

Actual samples of pyrolytic graphite, though fairly soft parallel to the predominant direction of the basal planes of the crystallites, tend to be much harder than would be indicated by the theoretical anisotropy ratio. Apparently, various kinds of lattice pinning and bonding between the layers prevent slip. The increasing availability of well-oriented graphites has brought to the fore the interesting possibility of substances which can unpin slip. Sorbed molecules of H_2O probably act in this way, since their removal markedly reduces the lubricating properties of polycrystalline graphite, for example when carbon brushes are exposed to reduced atmospheric pressures and low humidities at high altitudes. Halogens such as Br_2 and ICl also act as unpinning substances [6], and it may be assumed that many other intercalating molecules act in a similar way.

Compressibility. Graphite is very compressible normal to the network planes. Somewhat indirect estimates indicate a linear compressibility of graphite at ordinary temperatures of about $2{\cdot}6 \times 10^{-6}$ atm^{-1} [7, 8]. This is confirmed by observations on compacts of well-oriented graphite [22]. Parallel to the basal planes, the compressibility is too low to be measured. A probable value of the anisotropy ratio must be of the order 10^4 to 10^5.

Coefficient of thermal expansion. The anisotropy ratio of this property of graphite is fairly well known through the use of X-ray methods. At ordinary temperatures the thermal expansion normal to the basal plane is large; values of about 28×10^{-6} deg^{-1} seem likely. Parallel to the basal planes, estimates are rather indirect—the networks may even contract with rising temperature over a range of temperatures. Anisotropy ratios between 10^2 and 10^4 are likely. This property depends on lattice vibrations, so the ratio is likely to be strongly temperature-dependent [10].

Thermal conductivity. The values of this property depend on the nature of the energy carriers and on various ways in which their movement in a solid can be 'scattered'. Although graphite is a conductor of electricity, it has a ratio of charge carriers to atoms of only about 10^{-4}, compared with about unity in copper and about 10^{-8} in conventional semiconductors. Even in the most nearly perfect graphite, charge carriers are unimportant for thermal conductivity at ordinary temperatures, and about 99 per cent of heat transport occurs through lattice vibrations of different kinds [11, 12].

Because of the anisotropy of the lattice vibrations, the anisotropy ratio of thermal conductivity of near-ideal graphite may be as large as 200. The numerical value of this ratio depends on temperature, and it is also sensitive to imperfections of lattice vibration in the crystals. Figure 5 shows the anisotropy ratio found for a specimen of synthetic near-ideal graphite, produced from pyrolytic material by hot pressing and annealing [13]. For this material, at the optimum temperature, the thermal conductivity parallel to the basal planes is several times that of copper. In view of prospective uses of well-oriented graphite as a high-temperature material, it is important to determine whether any marked anisotropy of thermal conductance persists even up to 3000°C. Indirect determinations have been made in connection with the design of reactors manufactured from well-oriented graphite for use at very high temperatures. These results confirm that this anisotropy remains quite high, though exact values have not yet been obtained.

Electrical conductivity. All the electrical properties of pure graphite are conditioned by the fact that in the ideal crystals there is, at ordinary temperatures, only about one charge carrier for 10^4 atoms. In consequence, even a small concentration of defect sites capable of abstracting electrons or injecting them into the conduction band of the crystals can notably affect the total number of carriers, as well as their predominant sign. Sensitiveness of electrical properties to defect structures becomes even more prominent if the defects in question are bonded in some way to hetero-atoms.

Electrical conductivity, like thermal conductivity, shows marked anisotropy, as well as dependence on crystal imperfections. Early measurements on small natural crystals showed an anisotropy ratio as high as 10^4 at ordinary temperatures [14]. These measurements have been criticized on the basis that electrical measurements are difficult to make in the direction of the *c*-axis because of imperfect contacts due to the mechanical properties. Values of the anisotropy ratio as low as 200 have been reported, using larger natural specimens and procedures designed to avoid contact difficulties [15, 16]. However, numerous other measurements confirm the earlier order of magnitude [2, 17–19]. The use of large pieces of well-aligned graphites makes this measurement much more likely to be accurate.

The very high value of this anisotropy ratio stems from the unique electronic characteristics of graphite in the direction of the *c*-axis. In some ways the crystal behaves in this direction like a semiconductor, showing a positive temperature coefficient of electrical conductance. For near-ideal material, the resistivity in the ordinary range of temperatures is roughly halved for a rise of temperature of 250°C. On lowering the temperature, the anisotropy ratio increases. As with other properties of graphite, measurements of this anisotropy ratio to the highest attainable temperatures, near the sublimation point of carbon around 4000°C, could prove to have considerable technological potentialities as well as scientific interest. No data are yet available at such very high temperatures.

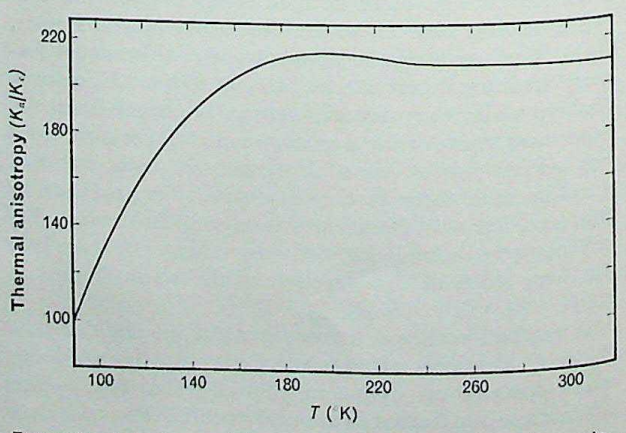


Figure 5 Anisotropy of thermal conductivity (K_a/K_c) of sample IFPA 57 plotted as a function of temperature.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Anisotropy of other electrical properties. With large specimens of well-oriented graphite now available, many other properties of electrically conducting crystals, such as the Hall effect, the magneto-resistance, the thermoelectric power, and various cross-interactions of thermal and electromagnetic parameters such as the Nernst-Ettinghausen effect can now be examined. In some cases anisotropies can be very large [19]. However, many of them present novel scientific problems in solid-state physics which cannot be discussed in the present article.

To give one illustration, in graphite the thermoelectric power S shows marked anisotropy. Even more unusual is the fact that S has, over a range of temperatures, opposite signs in the two principal crystal directions. The explanation of such highly unusual behaviour is not clear, but most probably there is more than one origin of thermal voltage gradients in the crystals, particularly if interaction between lattice vibrations and charge carriers is important. The thermoelectric power also depends on crystal defects in the graphite. Though the origin of the differences is not fully elucidated, it seems likely that the mean free path for charge carriers is very different in the principal crystal directions in graphite. Figure 6 shows some values for various graphites. These are not equal and are plotted as a function of their electrical resistivity to give some correlation with the crystal defects present in any specimen [22].

Some technological applications

Two technological developments may serve to point to the possibilities of using well-oriented graphite in work at very high temperatures.

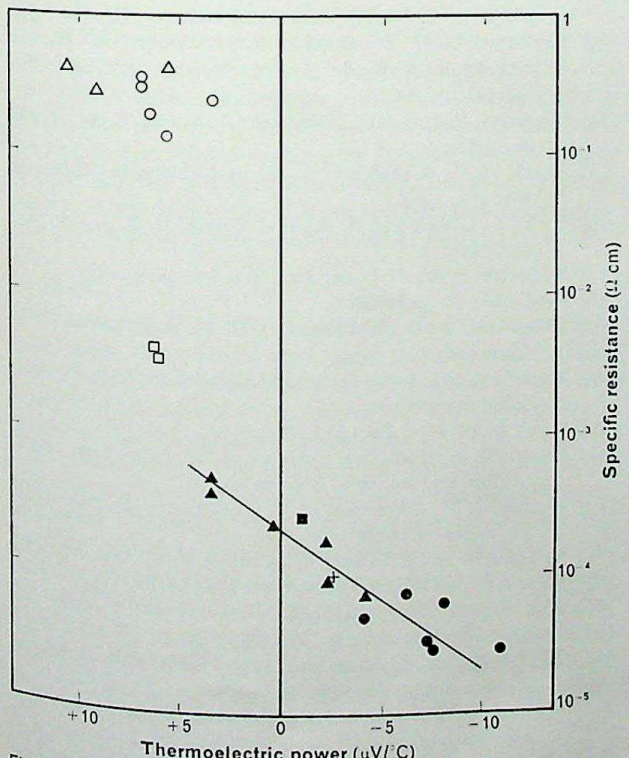


Figure 6 Empirical plot of thermoelectric power of various graphite specimens as a function of their specific resistance. ●, a-axis, pyrolytic M; ▲, a-axis, pyrolytic N; +, a-axis, natural Ceylon; ■, a-axis, compact; ○, c-axis, pyrolytic M; △, c-axis, pyrolytic N; □, c-axis, compacts.

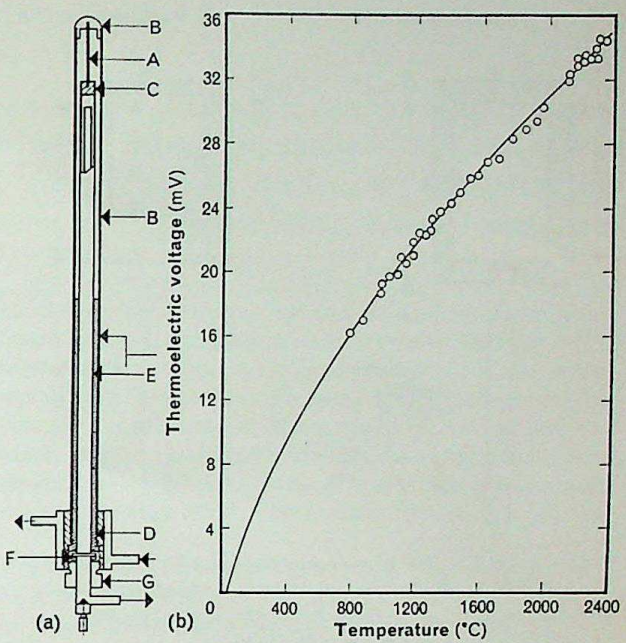


Figure 7 (a) Thermocouple: pyrolytic graphite (A), polycrystalline graphite (B), water-cooled brass-graphite junctions (C) and (D), compound asbestos insulation (E), helical spring (F) to allow for differential expansion, and ebonite plug (G) (overall length 50 cm approx.).

(b) Thermoelectric voltage (mV) as a function of temperature of anisotropic graphite thermocouple.

1. *An all-graphite thermocouple using the anisotropic thermo-e.m.f.* The high melting point of graphite, and its comparative inertness to many forms of chemical attack, make it a very desirable solid for the construction of thermocouples for use at very high temperatures. A novel development is to use the anisotropy to make both limbs of the same substance, cutting it in different crystallographic directions. One advantage of such a combination is that thermal diffusion of atoms at high temperatures cannot alter the composition of the solid at the hot junction. This avoids the gradual deterioration which is one of the difficulties that obstruct prolonged use of an alloy thermojunction. Further possible applications of thermojunctions consisting wholly of carbon may arise inside nuclear reactors. The use of graphite for measuring temperatures, or even as an auxiliary power generator, could avoid certain obvious difficulties with conventional heteroatomic thermojunctions.

As already stated, well-oriented graphite is rather weak with respect to shearing stresses parallel to the basal plane. In a practicable design of anisotropic thermocouple for use at very high temperatures this difficulty has been overcome by making one limb of an all-graphite thermocouple the outer sheath of the instrument [9]. This can be constructed of quite thick polycrystalline graphite, which is robust and durable. The inner limb of well-oriented graphite cut parallel to the *a*-axis joins it at the hot junction, and is thus well protected by the outer sheath. Other details of this design, together with a plot of its thermo-e.m.f. up to 2400°C, can be seen in figure 7. With modifications, such thermocouples should be practicable up to 3000°C or more.

2. *High-temperature chambers with walls of well-oriented graphite.* The striking anisotropy of thermal conductance of well-oriented graphite persists to a marked extent up

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

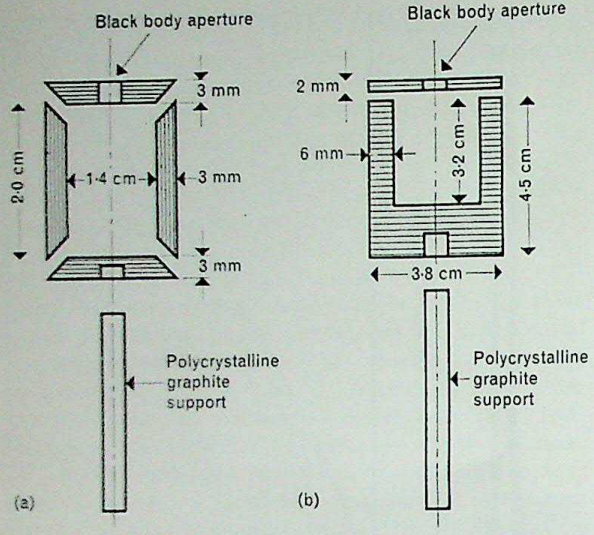


Figure 8 (a) Crucible of well-oriented pyrolytic graphite for work at 3000°C. (b) Crucible of well-oriented natural graphite for work at 3000°C. The lines on the crucibles show the direction of the *a*-axis of the crystallites.

to extremely high temperatures. This confers important practical advantages on its use as a wall material in high-temperature technology generally. Figure 8 illustrates some of the possibilities. It shows two effective designs of high-temperature chambers, with the orientation of graphite crystallites in either of the two principal directions [20]. As illustrated, the chambers are for use in an induction furnace, but similar principles apply for tubular furnaces with heating current supplied by electrodes.

When the *a*-axes lie parallel to the walls of the high-temperature chamber, as in figure 8a, the high thermal conductance in this direction results in unusually good uniformity of temperature within the chamber. In this connection, it is noteworthy that, for the best graphites, conductances may be expected to be several times higher than for the best alternative solids. Even more important for high-temperature technology generally is the low thermal conductance perpendicular to the chamber walls. This is so low that temperature gradients of 300°C or more per mm are readily maintained. For example, a crucible with walls 2·65 mm thick can be kept with its outer surface at 2100°C and with its inside at a uniform temperature of 3000°C. At these temperatures heat losses are mainly due to radiation. Stefan's T^4 law points to one great advantage of anisotropic graphite used in chamber walls. This is dramatically to reduce the wattage required for high-temperature enclosures heated electrically. The cleanliness, uniformity of temperature, and economy of power that can thus be achieved offer very great promise for basic scientific studies of properties of matter in the laboratory, particularly at temperatures above 2000°C. Technological developments of these principles of anisotropic design also seem promising.

When the heating is to be carried out by alternating currents of high amperage and low voltage, the walls of the well-oriented material are shaped so as to maximize the thermal insulation. But if the power is provided by induction heating, radiation losses can be reduced by generating the heat in the innermost layers of the anisotropic walls. To force the current inwards, split cylinder walls can be used with advantage (figure 9).

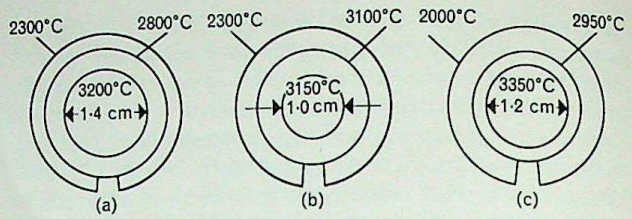


Figure 9 Temperature differences established across the walls of inductively heated susceptors screened with slotted pyrolytic graphite. (a) pyrolytic graphite susceptor, slotted shield 1·5 mm thick; (b) compacted natural graphite susceptor, slotted shield 2·5 mm thick; (c) pyrolytic graphite susceptor, slotted shield 3·5 mm thick.

Susceptors of well-oriented graphite in which the crystallites have their *c*-axes parallel to the walls can be made even more readily than the *a*-axis type. In the '*c*-axis type' of wall (figure 8b), temperature gradients down the wall can be made very high; but because of the high thermal conductivity parallel to the basal planes, temperature gradients are very low across them. This could be of particular value in certain uses of anisotropic graphite for refractories, for example in cooling high-temperature melts to produce certain types of ingots. Through developments of this kind, manipulations as well as measurements have been contrived on materials heated to above 3000°C [20, 21].

References

[1] Pirani, M. and Fehse, W. *Z. Elektrochem*, 29, 168, 1923.
[2] Brown, A. R. G. and Watt, W. 'Industrial Carbon and Graphite', p. 86. Society of Chemical Industry, London. 1958.
[3] Blackman, L. C. F., Dundas, P. H., Moore, A. W., and Ubbelohde, A. R. *Br. J. appl. Phys.*, 12, 377, 1961. (See also [5].)
[4] Blackman, L. C. F. and Ubbelohde, A. R. *Proc. R. Soc.*, *A*, 266, 20, 1962.
[5] Moore, A. W., Ubbelohde, A. R., and Young, D. A. *Ibid.*, *A*, 280, 153, 1964.
[6] Spain, I., Ubbelohde, A. R., and Young, D. A. *J. chem. Soc.*, 920, 1964.
[7] Bridgman, P. W. *Proc. Am. Acad. Arts Sci.*, 76, 9, 1945.
[8] *Idem. Ibid.*, 76, 55, 1948.
[9] Ubbelohde, A. R., Blackman, L. C. F., and Dundas, P. H. *Chemy Ind.*, 595, 1959.
[10] Bottomley, M., Parry, G. S., and Ubbelohde, A. R. (Unpublished observations.)
[11] Smith A. W. *Phys. Rev.*, 95, 1095, 1954.
[12] Powell, R. W. 'Industrial Carbon and Graphite', p.46. Society of Chemical Industry, London. 1958.
[13] Hooker, C. N., Ubbelohde, A. R., and Young, D. *Proc. R. Soc.* (In course of publication.)
[14] Ganguli, N. and Krishnan, K. S. *Nature, Lond.*, 144, 667, 1939.
[15] Primak, W. and Fuchs, L. H. *Phys. Rev.*, 95, 22, 1954.
[16] *Idem. Ibid.*, 103, 541, 544, 1956.
[17] Dutta, A. K. *Phys. Rev.*, 90, 187, 1953.
[18] Blackman, L. C. F., Saunders, G., and Ubbelohde, A. R. *Proc. R. Soc.*, *A*, 264, 19, 1961.
[19] Spain, I., Ubbelohde, A. R., and Young, D. A. (Unpublished observations.)
[20] Moore, A. W., Ubbelohde, A. R., and Young, D. A. *Br. J. appl. Phys.*, 13, 393, 1962.
[21] Ubbelohde, A. R., Young, D. A., and Moore, A. W. *Nature, Lond.*, 193, 571, 1962.
[22] Blackman, L. C. F., Dundas, P. H., and Ubbelohde, A. R. *Proc. R. Soc.*, *A*, 255, 293, 1960.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Heterogeneous catalysis

Digitized by Arya Samaj Foundation Chennai and eGangotri

D. A. Dowden

An understanding of catalysis is of fundamental importance to chemistry, and the modern theory of the mechanism of action of catalysts has been much assisted by studies of the structure of complexes. This article discusses the factors that are involved in catalysis by solids, and the light that recent work has thrown on the nature of the intermediate surface complexes.

The term catalysis was coined by Berzelius in 1836; it is said to occur if a process is speeded by entities which, ideally, are not themselves consumed. Early workers proposed that catalysis was effected by the formation of easily decomposed intermediate compounds between the catalysts (C) and the reactants (A, B), whereby the bonds in A and B are loosened and their rearrangement is facilitated:

$$\text{uncatalysed:}\quad A+B\rightarrow D \qquad \ldots.(1)$$

$$\left.\begin{array}{l}\text{catalysed:}\quad A+C\rightarrow AC\\ \qquad\qquad AC+B\rightarrow D+C\end{array}\right\} A+B+C\rightarrow D+C \qquad ..(2)$$

Their reasoning still stands, although progress in chemistry has given us a more sophisticated concept of a compound and has demonstrated that the intermediates may be fugitive. It was not possible to study catalysis quantitatively until Arrhenius had shown that reaction rate (r) always depends on the temperature T(°K).

$$r=ce^{-E/RT}f\,[\text{reactants and products}] \qquad \ldots.(3)$$

where c is a constant and E is the activation energy related to the energy needed to loosen the bonding in the reactants so as to attain the activated state; R is the gas constant. Ostwald suggested that catalytic action should be measured by the induced change in r.

In heretogeneous catalysis, the catalyst is a solid—for example, a metal, an oxide, a sulphide, a selenide, a halide, or a mixture of these—and interest centres upon the reactivities of the complexes formed at the surface of these solids. Complications arise because catalytic activity seems sometimes to be associated with special surface sites, called 'active' centres by H. S. Taylor [18].

Sorption

The molecules of all fluid substances are attracted by the solid phase, associating first with the exposed surfaces (adsorption) and afterwards, in some systems, with the interior of the lattice (absorption). There are two kinds of adsorption, physical and chemical.

Physical adsorption is sustained by physical forces alone, without any redeployment of chemical bonds. The weak interaction with the solid surface seldom distorts the adsorbed molecule sufficiently to make it more reactive. At low temperatures (80–90°K), multilayers of gas may be physisorbed. The volume of gas in a monolayer can be measured by analysis of the adsorption isotherm [1]. This provides a measure of the surface area of the solid. Chemical adsorption, on the other hand, is characterized by the formation of chemical bonds between the adsorbate (or its parts) and the atoms of the surface. This is the process by which the intermediate complexes are formed, and it is essential to heterogeneous catalysis. The activity of the catalyst will increase with its capacity to form the appropriate complexes, and will thus depend upon the specific area (m^2/g) and chemistry of its surface.

D. A. Dowden, *B.Sc.*
Was born in Bristol in 1914, and educated at Bristol University and Amherst College in the United States. He joined Imperial Chemical Industries Ltd in 1938. He has lately been elected to a new class of I.C.I. appointment—that of Senior Research Associate—designed for those who want to make their careers in research, spending the minimum time on administration. His particular research interest is the study of all aspects of catalysis.

The accessible surface of a solid

It is broadly true that the activity of a given mass of catalyst increases with its specific area. The most efficient catalysts, such as those used in industry as compacts of small particles or as porous solids, possess greatly extended surfaces (100–700 m^2/g) resulting from interstices and pores of small radius. The relationship has not been generally established over wide ranges of specific area because of the limitations to mass transfer in small pores, and because of the inherent difficulty of maintaining the chemical nature of the solid phases unchanged as the preparation of the catalyst is varied.

In fast gas reactions, such as oxidations, or in reactions where the catalyst is immersed in a liquid phase, diffusion to the envelope of the catalyst aggregate or within its pores may be slower than the uninhibited surface reaction. Under these conditions, the active surface in small pores is ineffective, and, in addition, the parameters of the rate equation and the catalyst selectivity differ from those due to chemical factors alone. The distribution of pore sizes is then one of the most important characteristics of a catalyst to be measured and adjusted [2].

A solid of large specific area must be composed of small particles ($10^{-7}-10^{-6}$ cm in diameter), and it may be either crystalline or amorphous. The high surface energy drives aggregation processes, such as crystal growth, at rates that are controlled by the mobility of the atoms of the lattice, and this mobility increases with decreasing melting point. Catalysts are therefore always made at the lowest possible temperatures by reactions involving the formation or transformation of solid phases. As a consequence, the resulting metastable lattices may be defective. Overheating and long use cause loss of activity by sintering and, possibly, by annealing of defects; active phases of low melting point—examples are most metals, V_2O_5, and $CuCl_2$—are therefore stabilized by adding refractory oxides, such as MgO and Al_2O_3, that have a high specific area.

The measurement of the exposed area of each phase present in a multi-component catalyst is difficult, but the specific adsorption of simple gases (H_2, CO) can provide a method for some solids, such as platinum.

The topography of the surface

It is helpful to distinguish good surfaces from bad. In this sense, a good surface is that which approximates closely

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

to the ideal, whereas a bad surface contains lattice irregularities.

Field-emission microscopy [3] and low-energy electron-diffraction (LEED) [4] give support, in general, to the model of the crystal surface proposed by the classical crystallographers. Emission microscopy can be used only with refractory metals, where it provides pictures of clean surfaces which show the atoms to be disposed much as expected for those in planes bounding the body-centred cubic lattice. LEED yields similar information even for solids of low melting point, providing they can be cleaned. It has revealed that atoms in the crystallographically simple surfaces of nickel and diamond are but slightly disturbed, lying closer to the penultimate layer than the unit cell dimension would indicate, whereas those of silicon and germanium have undergone rather more rearrangement to allow the saturation of broken bonds in pairs. The atoms of clean nickel surfaces are further rearranged on chemisorption of even such a loosely held gas as hydrogen; it is well known that extensive faceting occurs if single-crystal spheres of copper or oriented silver crystals are exposed during oxidation reactions.

On good crystals, active centres must be special crystal faces, edges, or corners. The non-peripheral atoms of a surface plane should be of equal potential activity before chemisorption. They will not necessarily be so afterwards —they may show induced heterogeneity.

Presumably, bad solids have bad surfaces, and these may therefore contain point defects, such as vacancies, interstitial atoms, kinks, corners, and emergent line dislocations, and line defects, such as edges, steps, screw dislocations, and grain boundaries [5]. Physical methods, such as those noted above, augmented by electron microscopy, the diffraction of electrons and X-rays, and auxiliary etching techniques, have demonstrated these defects in the surfaces of crystals of most classes of solid. However, little is known about their occurrence in small crystals or of their effects on catalytic activity in larger crystals. Since the 1920s, workers have speculated about these effects, but only the most advanced techniques are likely to produce unequivocal answers to this most important question.

H. E. Farnsworth and R. F. Woodcock have shown [6] that for ethylene hydrogenation on clean nickel, disordered surfaces are more active than annealed surfaces. On the other hand, other workers have found [7] that the rate of decomposition of formic acid on evaporated silver films is best related to the extent of the flat surface parallel to {111} planes. Amorphous solids and melts can show high activity, so that neither long-range order nor a type of line defect is everywhere essential for catalysis. The problem has no simple, general solution; all the defects listed may be active centres under some circumstances, and in practice all real solids are defective.

The chemistry of the surface

The reactivity of the virgin surface, as measured by chemisorption, must arise from the redeployment of saturated and unsaturated valencies by the surface atoms. In addition, these atoms may move to new positions. The catalytic activity of the surface is controlled by the bonding and the valencies of the asymmetrical complexes so formed, whether they are stable, unstable, or activated, and the principles to be applied are therefore not different from those of chemistry in general.

Even in Sabatier's time, the intermediate compound theory led, by analogy with homogeneous catalysis, to the classification of solid catalysts as acid-base or reduction-oxidation systems [8] and thus to a systematic discussion of selectivity in descriptive chemical terms. The notion of the near-invariance of bond-energy and bond-characteristics produced correlations between the properties of the bond M—X in the chemisorbed layer of X on M (solid) and in the solid MX. R. Schenck, among others, pointed out that the heats of formation of metal oxides were inversely proportional to the oxidation activity of the metals, and Dutch workers have recently noted [9] a similar connection between the stability of metal formates and the activities of metals and oxides in the decomposition of formic acid. These observations accord with the intuitive view that, for catalysis to occur, chemisorption must perturb the adsorbate molecule to some extent, but not sufficiently to form a very strong bond with the surface.

Rough estimates of these bond energies have been obtained for chemisorption on metals by adapting the methods used for molecules [10]. L. Pauling's well-known equation

$$E(A—C) = \tfrac{1}{2}[E(A—A) + E(C—C)] + 23{\cdot}06(x_a—x_c)^2$$

gives the bond energy $E(A—C)$ of a molecule AC, where A and C have electronegativities x_a and x_c respectively. This can be converted to the Eley-Stevenson equation

$$E(M—X) = \tfrac{1}{2}[E(M—M) + E(X—X)] + 23{\cdot}06(x_m - x_x)^2$$

where $E(M—M)$ is derived from the cohesive energy of the metal and x_m is about one-third of its work function. This and similar calculations are as yet of only academic value, as heats of chemisorption must still be measured. There is at present a renewed interest in such thermochemistry [11].

The broken bonds (M—) at solid surfaces have always been considered to have properties similar to those of the interior bonds, whether these be ionic, covalent, or metallic. At first, chemisorbed species were represented as ions on ionic lattices, and as radicals on covalent solids and metals [10]. The intermediate types tended to be neglected, although the electron-pair and dative bonds were distinguished, implying that covalent surfaces exposed arrays of unpaired spins (giant free radicals), lone pairs, and lone pair acceptors. Recent research on the magnetic properties of finely divided ferromagnetic metals [12], on the low temperature ortho-para hydrogen conversion [10], and on the modification of electron-spin resonance signals by adsorption of gases, supports the view that free valencies exist at the surfaces of pure solids. A strong indication of the presence of the expected donor-acceptor sp^3 surface orbitals (figure 1) is found in the properties of the {111} faces of the III-V semiconductors (those with wurtzite structure, such as InSb [19]). Unfortunately, formalized quantum-mechanical treatments of surface states have usually ignored the chemistry of the substance, but J. Koutecky's studies of diamond and graphite surfaces have remedied this omission for carbon [13].

If the solid is treated as an electron source or sink, the methods of solid-state physics can be used to study electron shifts in the dative and ionic bonds. The displacements of charge which occur on chemisorption

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

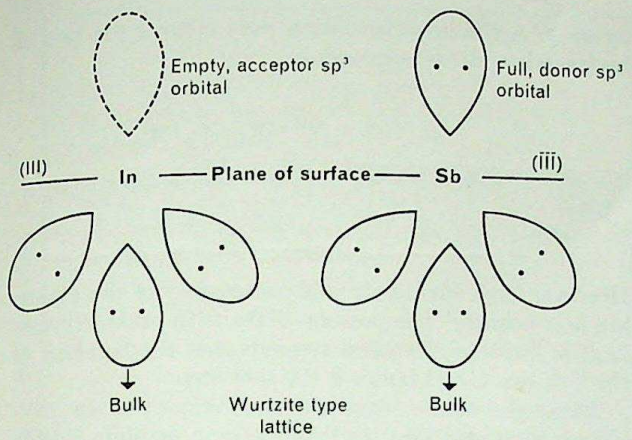


Figure 1 Donor-acceptor orbitals at III–V semiconductor surfaces.

produce localized surface dipoles (they will be negative side outward for electronegative adsorbates like oxygen) which have been measured in many systems through their effect on work functions, surface potentials, and resistivities.

Semiconducting solids show marked changes of resistivity when exposed to gaseous reactants during chemisorption and catalysis, and these effects remain the subject of much experiment and theory. *n*-type semiconductors, such as slightly non-stoichiometric zinc oxide, ZnO_{1-x}, conduct because quasi-free electrons are produced in the lattice by the easy ionization of the small concentration of interstitial, monovalent zinc ions. Chemisorbed oxygen traps conduction electrons in an electron-acceptor reaction, $Zn^{+}+O_2 \rightleftharpoons Zn^{2+}+O_2^{-}$, and the resistivity rises, but one form of chemisorbed hydrogen, perhaps $Zn^{2+}+O^{2-}+\frac{1}{2}H_2 \rightleftharpoons Zn^{+}+OH^{-}$, donates electrons and the resistivity falls. In *p*-type semiconductors, such as NiO_{1+x}, the current is carried by electrons hopping from normal lattice cations (Ni^{2+}) into 'holes' (Ni^{3+} ions produced by the slight oxygen excess). The chemical potential of electrons in *n*-type semiconductors is greater than in *p*-types (figure 2). These *n*-type semiconductors tend to be electron donors (reducing agents) and *p*-type semiconductors electron acceptors (oxidizing agents). The equilibria in the electron-transfer reactions are controlled by the electrostatic potentials set up between the trapped charge on the adsorbate and the space-charge due to the ionized donors or acceptors: the space-charge effects can be used to account for the decline in heats and rates of chemisorption with increasing surface coverage [10]. Alteration of the concentration and the chemical potential of electrons or holes in semiconductor catalysts must affect surface reactions, and additives having valencies different from the host lattice profoundly modify chemisorption and catalysis as well as resistivity.

Adsorbates, too, are classed as donors or acceptors, as also are reactions if the slow step can be recognized. However, the lack of a systematic catalytic chemistry renders these assignments equivocal and hinders the adoption of the established physico-organic nomenclature, such as induction and mesomerism, for organic reactions over catalysts.

The latest development in catalysis is the application of ligand field theory to the surface complexes [14, 15]. Semiconductor theory gives the energy of the electron levels involved in bonding; the new advance treats the symmetry and extension of the corresponding surface orbitals using molecular orbital methods. This facilitates the discussion of recently proposed surface species such as π-complexes, examples of which are carbonyl, olefinic, acetylenic, allylic, and aromatic complexes, and charge-transfer complexes. The great resources of co-ordination chemistry can now be applied to surface chemistry.

The intrinsic activity of surfaces

Insulators have much less activity in oxidation-reduction reactions than have conductors, although the distinction is not always sharp and diminishes at higher temperatures.

All active solids are acidic or basic to some degree, but the typical base is an alkaline earth oxide and the typical acid a congener of B_2O_3, SiO_2, or P_2O_5, in groups 3–5 of the Periodic Table. The high-area refractory oxides are the most useful as catalysts or as supports for mobile active phases. Although there is a general agreement that the solid catalysts function in the same way as conventional acids and bases, it is not clear whether proton switching mechanisms or electron-pair switching mechanisms are involved at the active centres. These two mechanisms are known respectively as Brönsted and Lewis mechanisms.

The best known oxides of acidic function are alumina, alumina-silica, magnesia-silica, and phosphates, such as $AlPO_4$. They usually contain a small residue of structural or added water, taken to be evidence of protonic acidity, and strongly chemisorb bases. The bases are thus catalyst poisons. The following processes for the dehydration of tert-butanol show the kinship with other protonic acids in different phases:

tert-BuOH + C ⇌ butene + H_2O + C					C = catalyst
gas (g)	g	g	g	g	C = HCl, HBr
liquid (l)	l	g	l	l	C = H_2SO_4, H_3PO_4
g	l	g	g	l	C = ditto in porous solids
g	s	g	g	s	C = Al_2O_3, Al_2O_3–SiO_2, $AlPO_4$

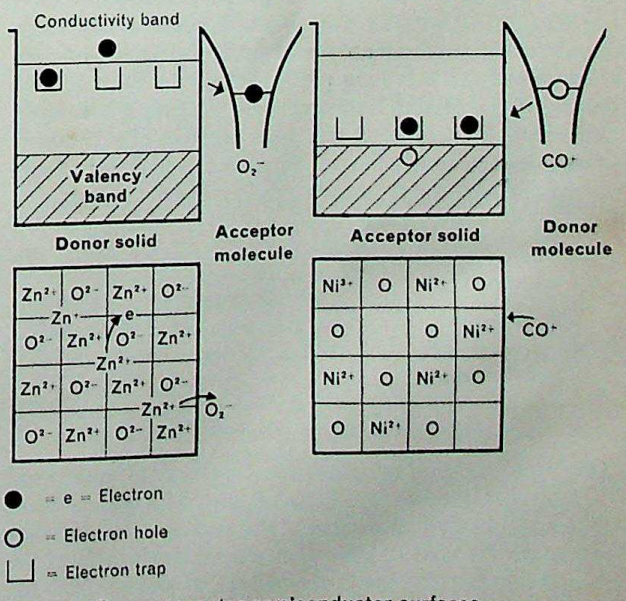
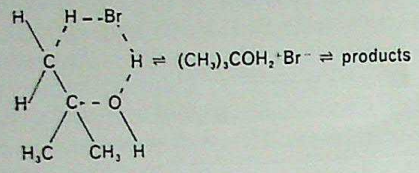


Figure 2 Donor-acceptor semiconductor surfaces.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

In the gas phase, the activated transition state seems to lie between I and II in the following equation [16]:



I II

but in polar solvents, the ion pair dissociates:

$$(CH_3)_3\overbrace{COH_2^+Br^-} \rightleftharpoons (CH_3)_3COH_2^+ + Br^-$$
$$(CH_3)_3COH_2^+ \rightleftharpoons C_4H_9^+ + H_2O$$

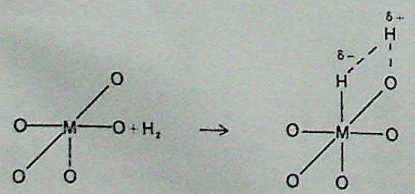
III

The isomerization, alkylation, polymerization, and cracking reactions of hydrocarbons appear to proceed through intermediates resembling carbonium ions (III). Electrostatic forces contribute to the binding energy of the ion in the gas phase, to its solvation energy in solution, and to its chemisorption on acidic oxides: similar progressions can be devised to illustrate the relation between Friedel-Craft catalysts and acidic oxides. However, the true nature (Lewis or Brönsted) of the active sites has not yet been established for all solids, despite the application of spectroscopy and electron-spin resonance. Lewis acid centres are more in evidence on alumina, but both kinds are found on alumina-silica and presumably contribute to reactions, giving carbonium ions, as do the powerful polarizing centres in molecular sieves.

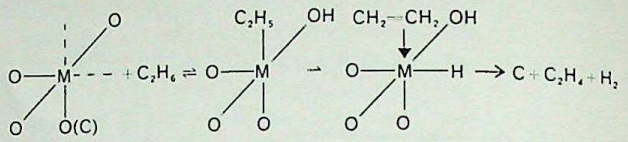
Little is known about bases; they chemisorb acids such as phenol, and catalyse reactions such as the aldol condensation in the gas phase.

The most effective redox catalysts are those containing the transitional elements of variable valency as oxides, sulphides, and halides. The active solids are often non-stoichiometric, and *d*-orbitals play a vital part in the bonding of the surface complexes.

Figure 3 shows the intrinsic activity of some oxides of the first long period in hydrogen-deuterium exchange ($H_2+D_2 \rightleftharpoons 2HD$) at 90°K, propane dehydrogenation at 600°C [15], and cyclohexene disproportionation at 200–500°C [17]. A similar twin-peaked pattern has been found for the hydrogenolysis of carbon disulphide over sulphides of the first long period at 200°C. Crystal field theory can be used to interpret these patterns if hydrogen chemisorption occurs on the (001) surfaces of substances of the NaCl structure in such a manner as to restore near-octahedral symmetry around the exposed cations:



The corresponding splittings of the 3*d* levels of the central cation, and empirical values of the splitting constant derived from optical spectra of the cation in appropriate solids, can be used to show that crystal field stabilization should increase the heats of adsorption, and possibly the rates of adsorption, over the outstanding catalysts of figure 3. A similar dissociation may control the rate of hydrocarbon dehydrogenation:



However, hydride-bonds and π-bonding of the olefine are now possible. The position of the twin peaks in cyclohexene disproportionation suggests that the breaking of the first two C—H bonds is the slow step.

Although halide catalysts are employed in oxychlorination reactions, and sulphates in sulphur dioxide oxidation, attention in this section will be directed to the oxides used in the total or selective oxidation of hydrogen and hydrocarbons. The compounds of transitional metals are always of outstanding activity, especially those of the first long period.

Three principal groups of oxides can be recognized:

(*a*) Oxides of high oxygen content, *p*-type or intrinsic semiconductors (Cr_2O_3, Mn_3O_4, Co_3O_4, NiO, CuO—the formulae are approximate); these are the most active and non-selective.

(*b*) the *n*-type semiconductors (V_2O_5, MoO_3, WO_3, Fe_2O_3); these are less active but more selective.

(*c*) Oxides of the elements of the b-subgroups, especially SnO, Bi_2O_3, SeO_2, and TeO_2; they are relatively inactive but highly selective.

Catalysts for total oxidation are often based on the oxides of class (*a*). Those for the selective oxidation of hydrocarbons, such as the oxidation of propylene to acrolein, or benzene to maleic anhydride, are based on the oxides of classes (*b*) and (*c*). Roughly the same patterns of activity are found in the oxidation of hydrogen and hydrocarbons and in the decomposition of nitrous oxide. Nitrous oxide decomposition on semiconductors has been represented as

$N_2O\ (g) \rightleftharpoons N_2O\ (a)$ $\quad a$ = adsorbed
$N_2O\ (a)$ + lattice electron $(e) \rightarrow N_2(g) + O^-\ (a)$
$O^-\ (a) \rightarrow \frac{1}{2}O_2\ (g) + e$
or O^- + electron 'hole' $\rightarrow \frac{1}{2}O_2\ (g)$

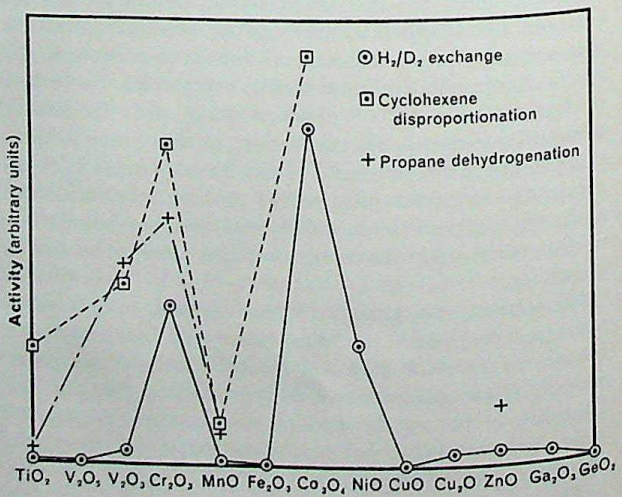

⊙ H2/D2 exchange
⊡ Cyclohexene disproportionation
+ Propane dehydrogenation
Activity (arbitrary units)
TiO2 V2O5 V2O3 Cr2O3 MnO Fe2O3 Co3O4 NiO CuO Cu2O ZnO Ga2O3 GeO2

Figure 3 Activity of oxides of the first long period.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

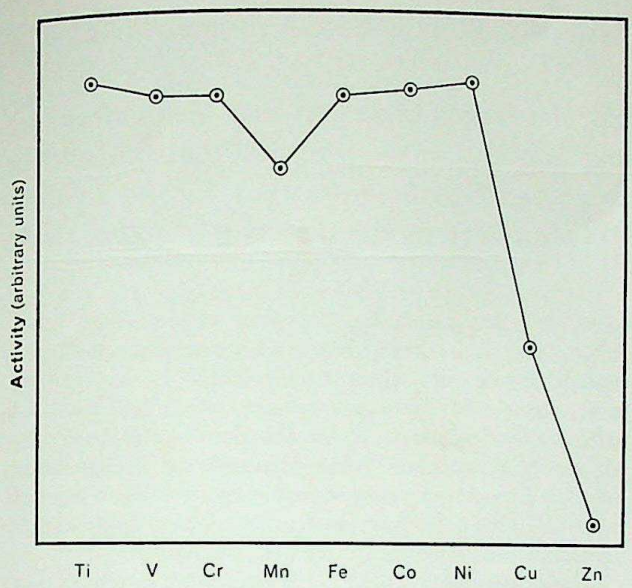
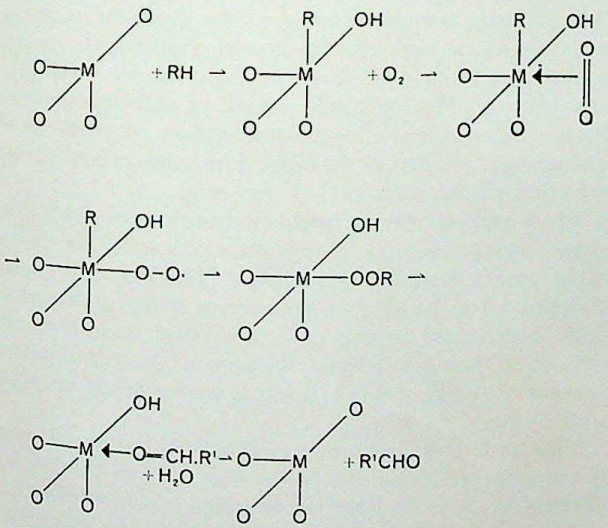


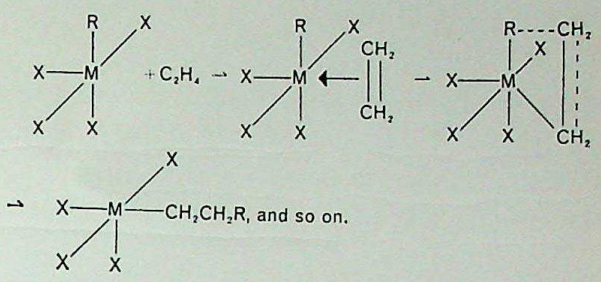
Figure 4 Activity of metals of the first long period.

in line with the electron displacements discussed earlier. The oxidation of hydrocarbons (RH) is closely related to dehydrogenation, and among the irreducible transitional oxides of the first long period the patterns of activity resemble one another. The following mechanism for oxidation with molecular oxygen can therefore be put forward:



If RH is unsaturated, as in the oxidation of propylene to acrolein, where the double bond must be preserved, there may be π-bonding of the olefine and the allyl radical to the cation.

The polymerization of alpha-olefines to linear molecules of high molecular weight is catalysed by compounds of transitional elements in low valency states. The Ziegler-Natta catalysts are formed from the halides of the metals of groups 4a to 6a in the presence of a metal alkyl. The Phillips–Standard Oil catalysts have as active species the oxides of chromium (Cr^{5+}) or molybdenum (Mo^{5+}), and they are probably related to the molybdenum catalysts which effect disproportionation of olefines and the hydrocondensation of carbon monoxide to polymethylenes. P. Cossee [20] has proposed a mechanism for olefine polymerization based on pi-complexes and an insertion mechanism.



From a tentative molecular orbital diagram for a typical octahedral complex, $RTiCl_4(C_2H_4)$, the geometrical and electronic states lead to the conclusion that central ions with configurations d^0 to d^3 should be the most effective.

Figure 4 shows that the activities of the metals of the first long period, in the interconversion of the para and ortho modifications of hydrogen, give a twin-peaked pattern with some resemblance to that of figure 3 [21]. Metallic Cu, Ag, and Au, with filled *d*-bands, are associated with the smaller activities in the reactions of hydrogen, such as olefine hydrogenation, and of oxygen, such as oxidation of carbon monoxide. The metals of group 8 are the most active of all solids in hydrogenation, oxidation, and more complex bond-splitting reactions. The small hydrogen chemisorption provides additional evidence of an activity minimum at manganese. In the same region, the electronic band structure of the metals varies rapidly, and bulk properties, such as the solubility of hydrogen and oxygen, pass through minima.

It appears therefore that valency considerations apply to metals just as to heteropolar solids and that the similar activity patterns of the two groups are related.

References

[1] Emmett, P. H. *Adv. Catalysis*, 1, 65, 1948.
[2] Wheeler, A. *Ibid.*, 3, 250, 1951.
[3] Brandon, D. G. *Endeavour*, 22, 90, 1964.
[4] Germer, L. H. *Physics Today*, 19, 1964.
[5] Van Bueren. 'Imperfections in Crystals'. North-Holland Publishing Co., Amsterdam. 1961.
[6] Farnsworth, H. E. and Woodcock, R. F. *Adv. Catalysis*, 9, 123, 1957.
[7] Bagg, J., Jaeger, H., and Sanders, J. V. *J. Catal.*, 2, 449, 1963.
[8] Sabatier, P. 'Catalysis in Organic Chemistry'. The Library Press Ltd, London. 1923.
[9] Mars, P., Scholten, J. J. F., and Zwietering, P. *Adv. Catalysis*, 14, 35, 1963.
[10] Hayward, D. O. and Trapnell, B. M. W. 'Chemisorption'. Butterworths, London. 1964.
[11] Gravelle, C. and Teichner, J. *J. chim. Phys.*, 61, 1089, 1964.
[12] Neugebauer, C. A. 'Structure and Properties of Thin Films'. Neugebauer, C. A., Newkirk, J. B., and Vermilyea, D. A. (Editors). John Wiley & Sons Inc., New York. 1959.
[13] Koutecky, J. *Kinet. Katal.*, 2, 299, 1961.
[14] Orgel, L. E. *Endeavour*, 22, 42, 1963.
[15] Dowden, D. A. and Wells, D. *Actes 2e Congr. Int. Catal.*, Paris, 1961.
[16] Maccoll, A. *Nature, Lond.*, 203, 809, 1964.
[17] Dixon, G. M., Nichols, D., and Steiner, H. *Proc. 3rd Int. Congr. Catal.* (To be published.)
[18] Schwab, G.-M. 'Catalysis' (translated by H. S. Taylor and R. Spence). D. Van Nostrand Co. Inc., New York. 1937.
[19] Lavine, M. C., Gatos, A. C., and Finn, M. C. *J. electrochem. Soc.*, 108, 974, 1961.
[20] Cossee, P. *J. Catal.*, 3, 80, 1964.
[21] Eley, D. D. and Shooter, D. *Ibid.*, 2, 259, 1963.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

The initiation of flowering

Digitized by Arya Samaj Foundation Chennai and eGangotri

Frank B. Salisbury

Many plants flower as a result of exposure to a particular length of day. It now seems clear that the length of day is measured by a light-absorbing pigment in the leaf, and that this releases a hormone that initiates the flowering. This article describes the work that has led to these conclusions, and to the separation of the pigment. It also suggests the direction of future work.

Perhaps the most fundamental problem of contemporary biology is that of the origin of form. We know that the genes control the ultimate form of the living organism, but since all the cells of an organism have the full complement of genes, we are perplexed by the manner in which certain genes are active only at certain times. In the growth of a plant, cells of the tip are continually dividing and enlarging and becoming specialized in such a way as to form stems and leaves. At a certain point in the plant's life cycle, however, other genes apparently become active so that these same cells develop, but into a highly modified version of the stem and leaves, the flower (figure 1). This redirection in growth apparently occurs in response to a chemical substance that is not synthesized in the dividing cells at the stem tip, but in the maturing leaves. This hormone, as yet uncharacterized, arises in many species in response to some external change in the environment. The manner in which morphogenesis may occur as directed by a flowering hormone, which in turn arises in response to environmental change, is the topic of this article [1–5]. We will consider four basic questions.

The environmental factors that cause flowering

The first clear answers regarding the light environment were put forth in a series of papers beginning in 1920, when the United States Department of Agriculture scientists, W. W. Garner and H. A. Allard [6], published a detailed investigation of factors that might cause soybean and Maryland Mammoth tobacco to flower under winter greenhouse conditions in Beltsville, Maryland. Temperature, nutrition, humidity, and light intensity were each carefully studied and eliminated, but it was found that both of the species would flower when the days were shorter than some maximum length, regardless of other conditions. Other species such as spinach (*Spinacia oleracea*), dill (*Anethum graveolens*), and henbane (*Hyoscyamus niger*) would flower only when the days were longer than some minimum. The first group of plants were called short-day plants and the second group long-day plants. The phenomenon itself was termed photoperiodism. Plants in a third category, which flowered under virtually any daylength condition, were called day-neutral plants (figures 2 and 3).

The picture has now become much more complicated [3]. For example, there are 'short-long-day' plants, which flower only when they are exposed to short days followed by longer days (as might occur in the spring), and there are also 'long-short-day' plants which flower in the autumn. There are even intermediate-day plants which flower only when the daylength is intermediate, and conversely there are plants which fail to flower when the daylength is longer than some value but shorter than another. Some plants flower in response to low (or rarely high) temperatures, instead of in response to daylength; yet others flower only as a consequence of a combination of temperature and daylength.

There are many interactions with other environmental factors, such as temperature, light intensity, and even factors such as soil nutrients and atmospheric humidity. Because of these many complications, most of the work has been concentrated on a few fairly straightforward species.

The way that the plant 'measures' daylength

This is quite clearly a physiological question. The initial clue came from recognition of the importance of the dark period. A few short-day plants (for example, the cocklebur *Xanthium pennsylvanicum*, and the Japanese morning glory *Pharbitis nil*) can be grown vegetatively under continuous light and then be induced to flower by exposure to only one dark period of sufficient length. Furthermore, a very brief interruption of moderately intense light applied at the right time completely nullifies the effect of this dark period (figure 3).

These and other experiments led workers in the period 1930–1950 to suggest that we should speak of long-night, rather than short-day plants. The long-day plants also proved to be short-night plants: if the dark period were interrupted in this case, flowering was promoted instead of being inhibited. However, the terminology was not changed, possibly because of the inertia usual in such matters.

This basic light-interruption observation opened up a world of possibilities. To begin with, it was possible to determine when the light interruption was most effective and how much light was required to bring about the response. It was also possible to find out which wavelengths of light were most effective in interruption of the dark period. Determination of this action spectrum, in which relative response is plotted as a function of wavelength, proved to be the most valuable experiment of all. It immediately became apparent that the resulting curve (figure 4), with its peak in the red region, closely resembled that already determined for other light-controlled systems, such as the germination of some light-sensitive seeds. This implied that the pigment system acting in photoperiodism was the same as that acting in other photo responses. There are also a number of blue-light responses, such as phototropism, which are apparently under the control of at least one other pigment system.

An extremely important discovery was reported in 1952 [7]. It was found that the effects of red light in promoting lettuce-seed germination could be completely

F. B. Salisbury, *B.Sc., M.A., Ph.D.*

Was born in Provo, Utah, in 1926, and educated at the University of Utah and the California Institute of Technology. He became Assistant Professor of Botany at Pomona College in California in 1954, and moved to the corresponding post in the Colorado State University in 1955. Since 1961, he has been Professor of Plant Physiology there. His particular research interests are the physiology of flowering, physiological ecology, and the biological problems of outer space.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

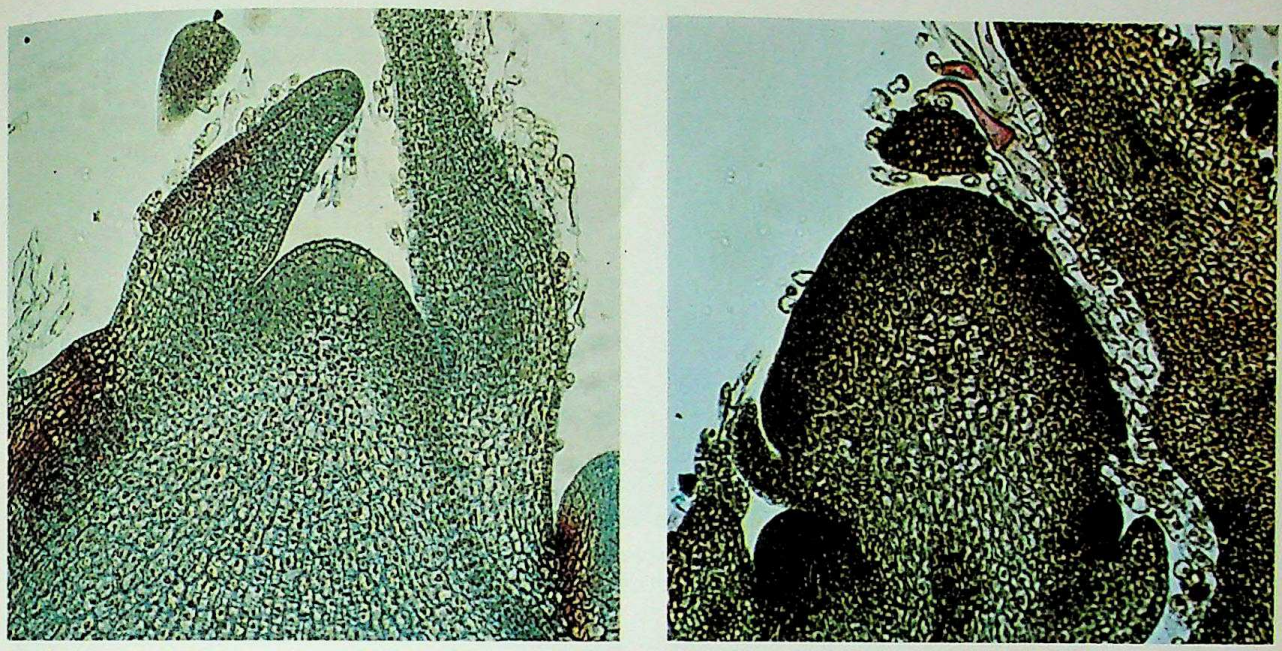
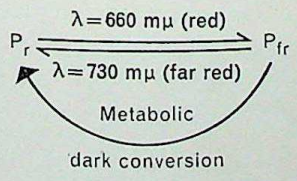


Figure 1 Longitudinal median sections of (left) a vegetative apical meristem of *Xanthium pennsylvanicum* Wall, and (right) an apical meristem which has begun to develop into a flower. Different stains were used in preparation of the two sections. (Both × 140)

reversed by subsequently exposing the seeds to light of longer wavelengths, in the far red. This reversal was also found to apply to photoperiodism and many other systems [8]. These results suggested that the pigment involved was converted from one form to another by absorption of red light and then back to the original form by absorption of far-red light. The reversal could occur a number of times, although in some systems other factors might limit the reversibility. Since a short-day plant is exposed to sunlight which is relatively rich in red before it is subjected to the extended dark period, and since this same light is effective in interruption of the dark period, it seems that the pigment must be converted in the dark from the far-red absorbing form, P_{fr}, to the red-absorbing form, P_r. These facts of conversion by red or far-red light and conversion in the dark are summarized by the following equation:



It soon became apparent that the far-red absorbing form of the pigment was the biologically active one, although the red-absorbing form could sometimes also play a role. For example, if a red-light interruption is given in the middle of the dark period, only a limited period of time (approximately 30 minutes in the case of the cocklebur) can be allowed to elapse before subsequent far-red illumination is completely unable to reverse the effect [9]. Apparently the pigment in the far-red absorbing form completes its inhibition during this time.

The pigment was finally isolated in the spring of 1959 [10]. This was a considerable achievement, firstly because it is present only in extremely small quantities, and secondly because measuring its optical absorption at one wavelength converts it to the form that absorbs at the other wavelength. These problems were solved, and the pigment has been directly demonstrated in many species of plants. The importance of this achievement for photobiology should not be underestimated.

The discovery of the reversible pigment system, named by its extractors phytochrome, seemed to solve many of the problems of photoperiodism. For example, the manner in which the plant might measure the length of the dark period might simply be a function of the dark-conversion times for the pigment system. If the critical dark period for cocklebur is 8 hours and 30 minutes, then one might say that 8 hours and 30 minutes are required for the inhibitory P_{fr} to be removed from the plant by dark conversion [11].

The role of phytochrome in photoperiodism is still considered to be paramount, but the picture has become very complicated. The idea of phytochrome conversion as a measure of time proves to be an insufficient one. Firstly, time measurement under threshold light conditions—light of an intensity such that it inhibits flowering slightly but not completely—is studied by determining the minimum time required for the first perceptible initiation of flowers. This time is called the critical dark period or the critical night. Threshold light does not extend this time (figure 5), although under these conditions the inhibition of flowering implies that phytochrome is not converted completely to the P_r form.

Secondly, there are many analogies in the flowering process to other rhythmic processes in both plants and animals. These correlations are impressive, and the idea that time measurement in the flowering process may be performed by the same biological clock that controls other rhythms seems quite reasonable. The results of a representative experiment, performed by Karl Hamner [12] and his colleagues at the University of California in Los Angeles, are illustrated in figure 6.

Thirdly, time measurement in the flowering process, as well as in the other rhythms, is very insensitive to temperature changes, although many aspects of the

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

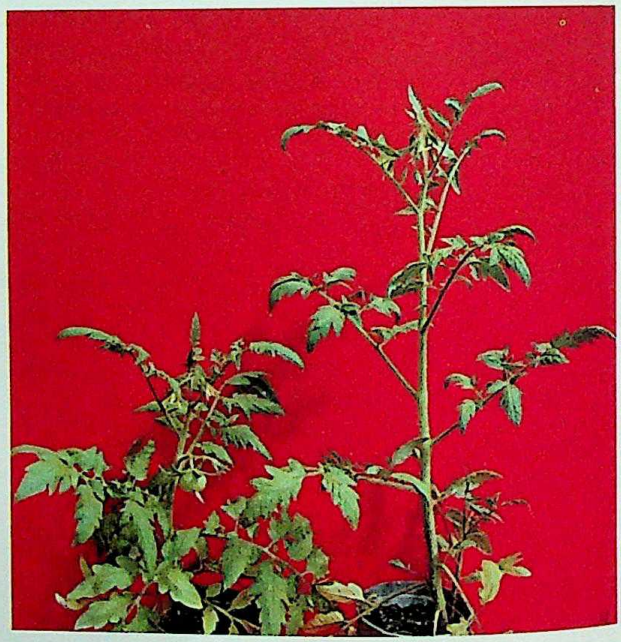
Digitized by Arya Samaj Foundation Chennai and eGangotri

Figure 2 Some representative plants and their response to short days and long days. Age of the plants at time of photograph is indicated.

Henbane *(Hyoscyamus niger)*, about 110 days old. (Left) short day; (right) long day.

Barley *(Hordeum vulgare)*, about 35 days old. (Left) short day; (right) long day.

Pigweed *(Amaranthus* sp.*)*, about 110 days old. (Left) short day; (right) long day.



Tomato *(Lycopersicon esculentum)*, about 110 days old. (Left) short day; (right) long day.

Cocklebur *(Xanthium)*, about 60 days old. (Left) short day; (right) long day.

Japanese morning glory *(Pharbitis)*, about 35 days old. (Left) short day; (right) long day.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

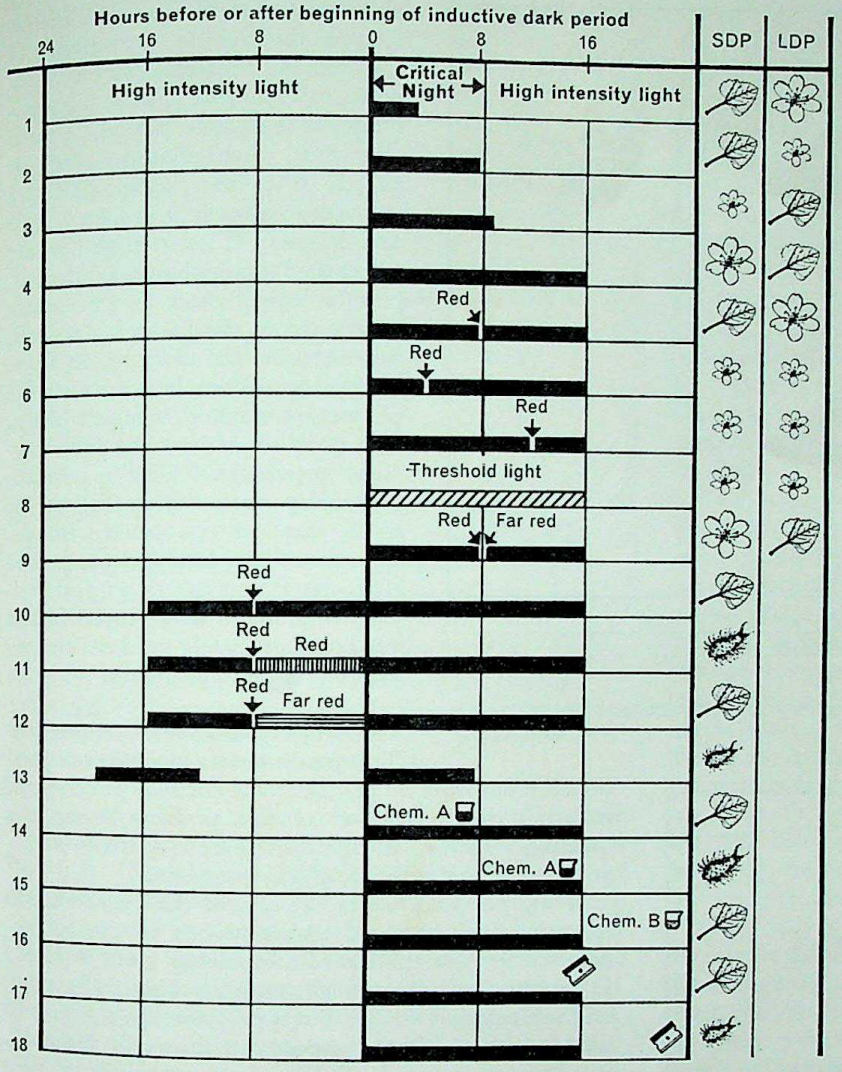


Figure 3 A summary of a number of photoperiodism experiments. (1) A dark period shorter than the critical night induces flowering in long-day plants (LDP) but keeps short-day plants (SDP) vegetative. (2 and 3) As the dark period just approaches the critical night-length, long-day plants flower slightly and as it just exceeds the critical night-length, short-day plants flower slightly. (4) An extended dark period causes profuse flowering of short-day plants but keeps long-day plants vegetative. (5) If the dark period is interrupted with red light near the critical night, short-day plants are inhibited in their flowering and long-day plants are promoted. (6 and 7) If the interruption comes at some other time, flowering may be inhibited or promoted in both response types but to a lesser degree. (8) Under so-called threshold light conditions, flowering of short-day plants is quantitatively inhibited and that of long-day plants is quantitatively promoted. (9) The effects of a red interruption are overcome by subsequent exposure to far-red light. (10) This and the following experiments all refer to cocklebur (and, in specific instances, a few other plants). If a light flash is given after 7½ hours (close to the critical night), a subsequent dark period is ineffective even though it is very long (as the light interruption becomes shorter and shorter, the dark period required for a minimum of flowering becomes longer and longer). (11) If this initial dark period is followed by red light, then a subsequent dark period is very effective. (12) If far-red light is used instead, the dark period is not effective. (13) If the light period following the first dark period is 12 hours long, conditions are apparently so optimal that a subsequent dark period shorter than the critical night will still induce flowering. (14 and 15) Some chemicals when applied to the plant (by dipping the leaves in a solution of the chemical), will inhibit flowering when they are applied before the end of the critical night, but not when they are applied after the end of the dark period. (16) Other chemicals will inhibit flowering even when they are applied some time after the dark period. (17 and 18) If the leaves are removed immediately following the end of the dark period, plants remain vegetative, but if some 8–20 hours are allowed to elapse, plants flower.

flowering process, including phytochrome conversion, are highly temperature-sensitive. Figure 7 shows the critical dark period determined for the cocklebur and the Japanese morning glory at various temperatures. The effect of temperature upon time measurement is very slight with the cocklebur, but appears to be quite large for the Japanese morning glory. Yet when time measurement is determined not by measurement of the critical dark period, which could be influenced by other factors, but by the time of maximum sensitivity to a light interruption, then time measurement is unaffected by temperature in Japanese morning glory also (figure 8).

Fourthly, a number of recent experiments from various laboratories, each carried out in a different way, seems to indicate that there are two phases to the flowering process, one of which is inhibited by red light and the other of which is promoted by red light [13, 14, 15; but see 16]. This would imply, if the effects are always *via* the phytochrome system as all the evidence indicates, that P_{fr} is essential for flowering at one time during the cycle and inhibitory to flowering at another. This is another close analogy to the other rhythms; light may inhibit a rhythm at one time and promote it at another. This is true of both plants and animals, including many organisms in which phytochrome is clearly absent.

Figure 3 illustrates the basic approach that we have taken at Colorado State University. Plants are left in continuous light for a few days and then given a dark period of 7½ hours—too short for the initiation of flowering. Following this dark period, they are given a brief interruption of light, normally quite inhibitory to the flowering process, and then after special experimental treatment, they are given a dark period of length sufficient to initiate flowering. The special treatments may consist of light periods of various durations, intensities, or qualities. The idea is to try to discover the conditions that will overcome the inhibitory effects of the 7½ hour dark period and the short-light interruption. Our results so far indicate that a light period of approximately 8 hours works well; that 12 hours is optimal and so effective that less than 8 hours of darkness following this will initiate flowering; that intensity during this 8 hours is of

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

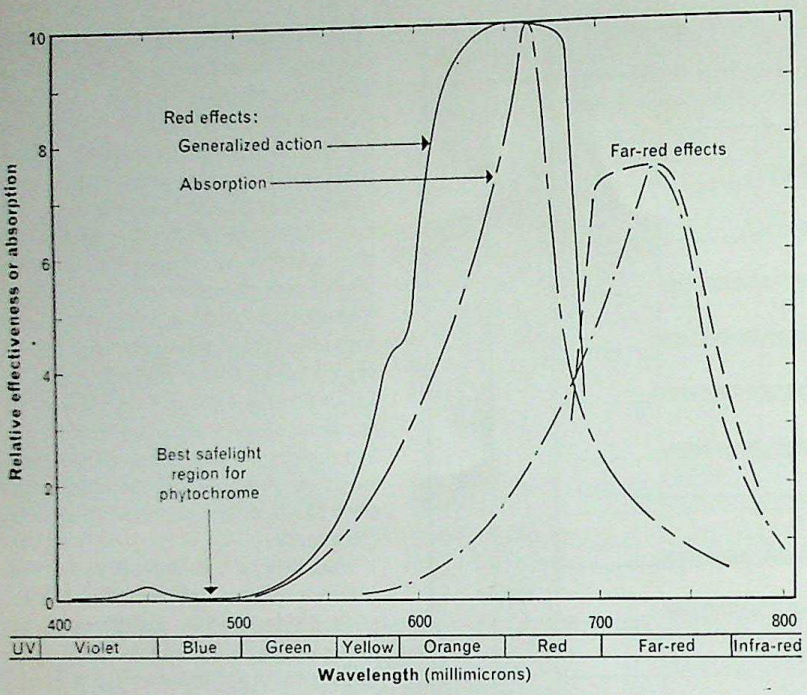


Figure 4 Action spectra for the red and far-red responses controlled by phytochrome [11].

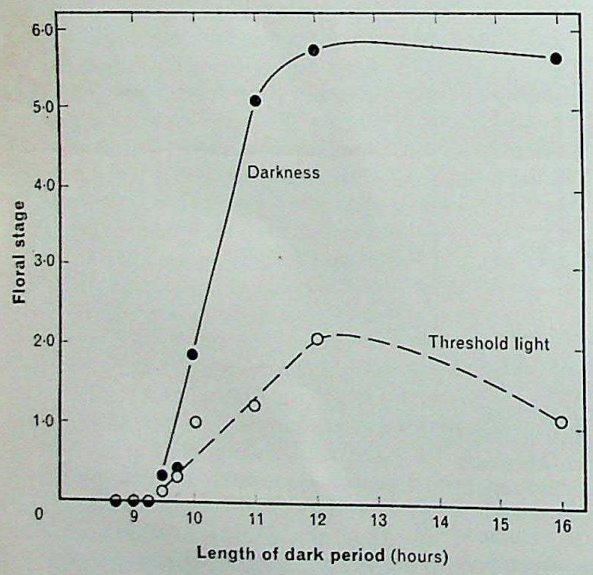


Figure 5 The critical night (as determined by exposing plants to dark periods of different lengths) is not changed when plants are maintained under threshold light, although flowering at longer night lengths is strongly inhibited [3].

secondary importance at best; and that red light is by far the most effective during this period and far-red light is inhibitory.

All of this clearly demonstrates the importance of the light period as well as of the dark period. Some plants, such as the cocklebur and the Japanese morning glory, appear to be brought to a state during the light period that they will remain in during many subsequent hours or even days of continuous light. When plants are finally placed in the dark, they will complete the cycle and thus respond to a single dark period. Yet both parts of the cycle are equally indispensable to the ultimate flowering response, and with many other species (such as the soybean) both phases of the cycle must match a cycling, light-dark environment tuned approximately to a 24-hour period. It turns out, thus, that photoperiodism is exactly what the name implies, a response to a periodic cycling of light and darkness. It is fortunate that the 'short-day' terminology was retained.

A biological clock [17] is clearly implicated in the flowering process. Furthermore, the clock seems to be coupled to the environment *via* the phytochrome system in higher plants. The question of how the same pigment system can inhibit or promote depending upon the cycling of the clock, must be connected with the question of how long-day plants and short-day plants can be so diametrically opposite in their responses and yet both ultimately produce the reproductive floral structure.

The immediate initiation of flowering

This proves to be a biochemical question. Recent work on phytochrome chemistry is essential to our ultimate solution of this problem, tying this question into the last one. But there is much to do beyond studying the nature of phytochrome.

It was shown towards the end of the 1930s that in flowering it is the leaf that responds to the 'photo-environment'. If the leaf of a cocklebur plant is placed in a dark bag for the requisite number of hours, the plant will subsequently flower, but if only the tip, the part of the plant that ultimately becomes a flower, is darkened, no response occurs; nor is there any response if only the stem is darkened. This suggested that a chemical stimulus was produced in the leaf and translocated to the bud

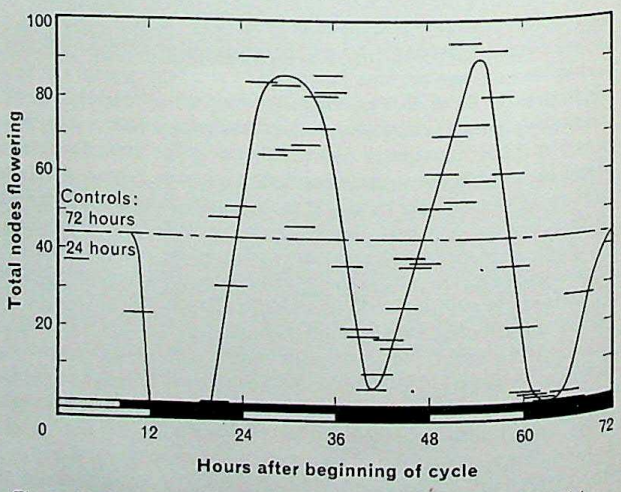


Figure 6 Responses of Biloxi soybean plants to 4-hour light interruptions given at various times during a 72-hour cycle. The lines indicate the 4-hour interruption periods. The upper bar on the bottom of the graph indicates the 8 hours of light and the 64 hours of darkness given in each of the 7 cycles to which the plants were exposed. The lower bar indicates the daily cycle of light and darkness under normal conditions [12].

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

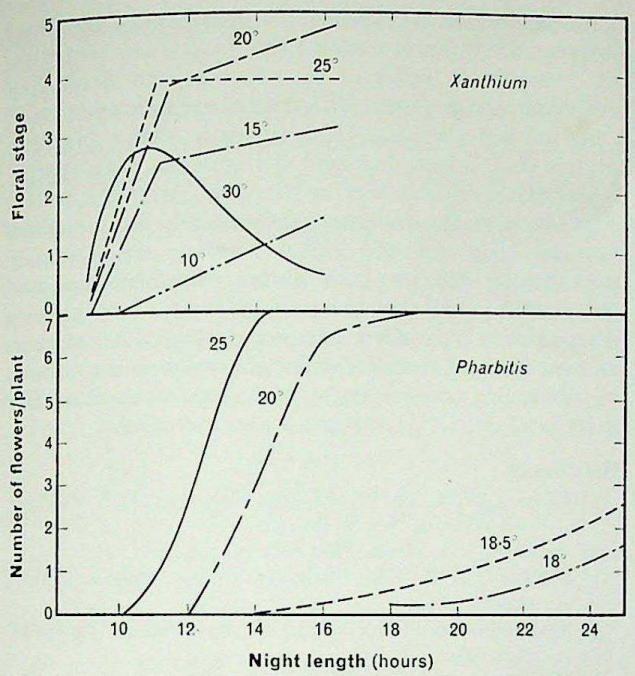


Figure 7 Responses of *Xanthium* (cocklebur) and *Pharbitis* (Japanese morning glory) to nights of different lengths applied at different temperatures [3]. (*Pharbitis* data from Hamner and Takimoto, personal communication.)

to initiate flowering there. In conjunction with these experiments by K. C. Hamner and J. Bonner [18], and by M. K. Chailakhyan [19], who called the hypothetical hormone florigen, it was also shown that the flowering stimulus could be translocated from one plant to another across a graft union. More recently, experiments have been performed in which the rate of movement of the flowering hormone from the leaves of certain plants can be measured, by removing these leaves at various times after a single inductive dark period.

This situation has, however, also become somewhat more complicated. Inhibiting compounds have been implicated in many cases rather than a hormone promoting flowering, and the interaction of these compounds with promoting compounds may well be the rule [5].

The most direct way to study the flowering hormone would be to extract it from the plant, analyse its chemical structure, and study its synthesis. To do this, however, we must be able to detect it. The only method available is that of applying a suspected substance to a vegetative plant, and causing it to flower. So far success in this kind of experiment has been meagre.

In 1961, R. G. Lincoln, D. L. Mayfield, and A. Cunningham [20] claimed success. They extracted cocklebur plants with alcohol at very low temperatures. Their results are not spectacular, in that the extracts produce only very early stages of flower development, but have been substantiated by D. J. Carr [21] in Belfast. The active fraction of these extracts is acidic, and Lincoln named his active substance florigenic acid [22].

It was shown by A. Lang [23] that certain plants that normally require low temperatures or long days for flowering would flower at high temperatures or short days when they were treated with gibberellins. How this relates to the overall problem of the physiology of flowering remains to be seen. In one very real sense, these compounds are the nearest to flowering hormones that have been extracted from a higher plant. They can be extracted from flowering long-day plants, or cold-requiring plants, in quantities sufficient to cause similar plants to flower under non-inductive conditions.

In spite of this, the gibberellins are probably not the postulated florigen [24]. For example, they will not remove the need for a short day. However, an applied compound which mimics the effect of the flowering hormone in some special way, or even leads to its synthesis in the plant, could be of tremendous commercial importance even if it did not solve the basic questions.

Because of the difficulties involved in extraction, we have taken a different approach [25]. We have searched for compounds that, when applied to the intact plant, inhibit the flowering process. Knowing how these compounds work in other biological systems, we have drawn some conclusions about the biochemistry of flowering. Our approach has involved three essential steps. In the first, a survey is made by applying potential inhibitors over a range of concentrations. Compounds which are found to be effective are then studied in a series of experiments designed to pinpoint the stage of the flowering process that they inhibit. For example, they are applied at various times before, during, and after a single inductive cycle (figure 3). Finally, if the compound which we are studying is an antimetabolite, then we attempt to reverse its inhibitory effect by simultaneously applying the suspected metabolite in solutions of increasing strength (figure 9). The results of these studies have also become increasingly complex over the years, but a few conclusions [3, 26] may be of interest.

Biosynthesis of flowering hormone. Dinitrophenol inhibits the formation of the flowering hormone. This suggests that respiration, and its product ATP, are required, as might be expected. At least two anti-amino acids (ethionine and *p*-fluorophenylalanine) inhibit hormone synthesis in cocklebur, and both are reversed by their corresponding metabolites (methionine and phenylalanine). A number of other anti-amino acids fail to have any inhibitory effects. Certain compounds that inhibit the formation of nucleic acids have also been effective in these experiments [27–29]. Some of these are at least partially reversed by their corresponding metabolites, but there is a very perplexing complication. Some are

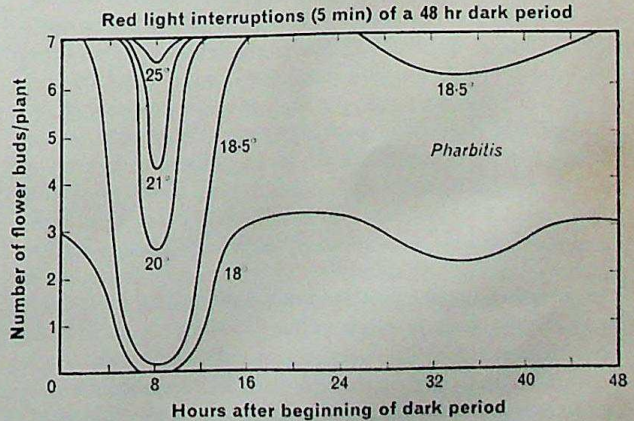


Figure 8 In spite of the strong effects of temperature upon critical dark period in *Pharbitis* (Japanese morning glory), time measurement is still seen to be independent of temperature. (Data from Hamner and Takimoto, personal communication.)

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

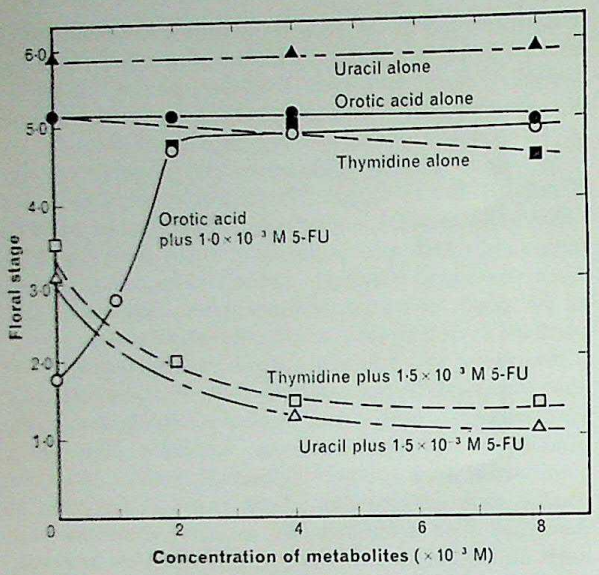

Uracil alone
Orotic acid alone
Thymidine alone
Orotic acid
plus 1·0 × 10 ⁻³ M 5-FU
Thymidine plus 1·5 × 10 ⁻³ M 5-FU
Uracil plus 1·5 × 10 ⁻³ M 5-FU
Floral stage
Concentration of metabolites (× 10 ⁻³ M)

Figure 9 Reversal of 5-fluorouracil (5-FU) inhibition by application of orotic acid. Thymidine and uracil fail to reverse (they appear to enhance somewhat) the inhibition due to 5-fluorouracil [3].

much more powerful inhibitors of flowering when they are applied to the bud than when they are applied to the leaf. Their effectiveness in the leaf however, can also be demonstrated.

Tris (2-diethylaminoethyl) phosphate, an antisteroid compound, also inhibits flowering [28]. It would be exciting to think that the flowering hormone might be a steroid, since many animal hormones are steroids. Unfortunately, attempts to reverse this inhibition have failed, and the inhibition itself occurs only very early in the dark period, some hours before hormone synthesis has begun. Its effect could be upon some early precursor, rather than upon the final steps of hormone synthesis.

Translocation of the hormone from the leaf to the bud. Plant stem-growth hormones, auxins, as well as certain compounds inhibiting the formation of nucleic acids, inhibit the flowering process when they are applied after hormone synthesis is complete, but before the hormone has arrived at the bud. The meaning of these observations eludes us.

Transformation and development of the bud. Certain herbicides will stop the development of the bud at any time. In addition, it has been shown that a nucleic-acid inhibiting compound (5-fluorodeoxyuraidine) that inhibits cell division (as demonstrated for the Japanese morning glory) also inhibits flowering, provided that it is allowed to act during the time when the flowering hormone arrives at the meristematic cells in the bud [29]. This shows that the nucleic acid synthesis of cell division is required if the flowering hormone is to act.

The response of the meristematic cells to the hormone responsible for flowering

Morphologically, the transition cells just below the central mother cell zone are the first ones to become active upon arrival of the flowering hormone (figure 1). Perhaps the best morphological description comes from investigators in Paris, and in Liège [30]. They recognize, for example, a series of phases from the developing embryo in the seed to the final developing flower.

At the histochemical level, it can be shown [31] that protein and ribonucleic acid synthesis increases sharply upon arrival of the flowering hormone, as though certain genes in control of this synthesis were being activated. Certain basic proteins called histones are especially prevalent in the cytoplasm during transformation, and this could be related to the gene activation. Starch grains disappear shortly after transformation. The electron microscope [32] reveals a striking increase in the number of ribosomes, concurrently with transformation. The activity of the Golgi apparatus also increases.

References

[1] Hillman, W. S. 'The Physiology of Flowering'. Holt, Rinehart, and Winston, New York. 1962.
[2] Lockhart, J. A. *Handb. PflPhysiol.*, 16, 390, 1961.
[3] Salisbury, F. B. 'The Flowering Process'. Pergamon Press, Oxford. 1963.
[4] 'Symposium on Flower Induction'. *Abstr. 10th Int. Bot. Congr.*, 187, 1964.
[5] Zeevaart, J. A. D. *Science*, 137, 723, 1962.
[6] Garner, W. W. and Allard, H. A. *J. agric. Res.*, 18, 553, 1920.
[7] Borthwick, H. A., Hendricks, S. B., Parker, M. W., Toole, E. H., and Toole, V. K. *Proc. nat. Acad. Sci., Wash.*, 38, 662, 1952.
[8] Borthwick, H. A., Hendricks, S. B., and Parker, M. W. *Ibid.*, 38, 929, 1952.
[9] Downs, R. J. *Plant Physiol.*, 31, 279, 1956.
[10] Butler, W. L., Norris, K. H., Siegelman, H. W., and Hendricks, S. B. *Proc. nat. Acad. Sci., Wash.*, 45, 1703, 1959.
[11] Hendricks, S. B. and Borthwick, H. A. 'Environmental Control of Plant Growth' (edited by L. T. Evans), p. 233. Academic Press, New York. 1963.
[12] Hamner, K. C. *Ibid.*, p. 215.
[13] Borthwick, H. A. and Downs, R. J. *Bot. Gaz.* (In press.)
[14] Meijer, G. *Acta bot. néerl.*, 8, 189, 1959.
[15] Könitz, W. *Planta*, 51, 1, 1958.
[16] Kofranek, Anton M. and Sachs, R. M. *Amer. J. Bot.*, 51, (5),520, 1964.
[17] Bünning, E. 'Die physiologische Uhr'. Springer-Verlag, Berlin. 1963.
[18] Hamner, K. C. and Bonner, J. *Bot. Gaz.*, 100, 388, 1938.
[19] Chailakhyan, M. K. *Dokl. Akad. Nauk, SSSR*, 3, 442, 1936.
[20] Lincoln, R. G., Mayfield, D. L., and Cunningham, A. *Science*, 133, 756, 1961.
[21] Carr, D. J. *Commun. 10th Int. Bot. Congr.* 1964.
[22] Lincoln, R. G. *Abstr. 10th Int. Bot. Congr.*, 189, 1964.
[23] Lang, A. *Proc. nat. Acad. Sci., Wash.*, 43, 709, 1957.
[24] Lang, A. and Reinhard, E. *Adv. Chem. Ser.*, 28, 71, 1961.
[25] Salisbury, F. B. 'Recent Advances in Botany', p. 1294. University of Toronto Press, Toronto. 1961.
[26] Collins, W. T., Salisbury, F. B., and Ross, C. *Planta*, 60, 131, 1963.
[27] Salisbury, F. B. and Eichhorn, G. L. *Ibid.*, 60, 145, 1963.
[28] Bonner, J., Heftmann, E., and Zeevaart, J. A. D. *Plant Physiol.*, 38, 81, 1962.
[29] Zeevaart, J. A. D. *Ibid.*, 37, 296, 1962.
[30] Bernier, G., Nougarède, A., Bronchart, R., and Rondet, P. *Rev. gén. Bot.* (In press.)
[31] Gifford, E. M. and Lance-Nougarède, A. *Abstr. 10th Int. Bot. Congr.*, 293, 1964.
[32] Jensen, W. and Healey, P. *Commun. 10th Int. Bot. Congr.*, 1964.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

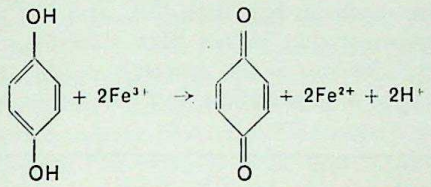
Quinones as biological catalysts

Digitized by Arya Samaj Foundation Chennai and eGangotri

R. A. Morton

Quinones occur naturally, and because they can easily be reduced, and the product easily oxidized, they can take part in the chain of reactions by which energy is made available. This article describes two families of quinones, the ubiquinones and plastoquinones, and also vitamin K, essential to the clotting of blood, which belongs to a related family of naphthoquinones.

Quinones are important in biological systems because of the ease with which they can be reduced to quinols, and quinols oxidized to quinones. The oxidation of hydroquinone

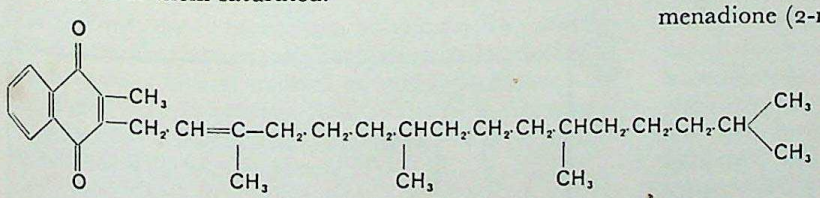


can be generalized

$$XH_2 \rightleftharpoons X + 2e + 2H^+$$

and the process is seen to result in loss of H^+ ions and electrons. The normal electrode potential E_0 falls from 0·715 volts for 1,4-benzoquinone to 0·484 volts for 1,4-naphthoquinone, and 0·154 volts for anthraquinone. The introduction of alkyl, alkoxy, and hydroxy groups reduces the redox potential.

Quinones made their first major impact on biochemistry with the discovery 30 years ago of vitamin K. In constitution it is a 2-methyl naphthoquinone with a 3-phytyl side-chain, a phylloquinone. Phytol, $C_{20}H_{39}OH$, is a mono-unsaturated alcohol best known because it occurs in chlorophyll. It contains four isopentenoid units, three of them saturated.



Vitamin K_1 (phylloquinone)

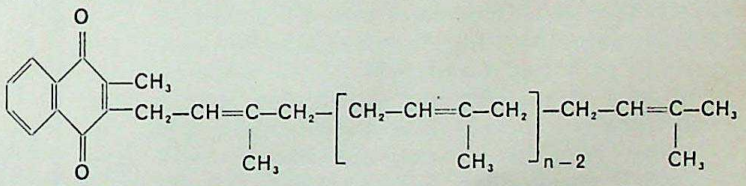
This vitamin was recognized by the effects produced by a deficiency; the primary symptom is a decrease in the concentrations of certain plasma proteins, including prothrombin, which are concerned in the coagulation of blood. Young chickens carry only small reserves of the vitamin, and on a suitable diet they are readily depleted. There is therefore a tendency to bleeding, brought about by changed coagulation properties of the blood. Biological assays make use of the blood clotting time; this is lengthened in deficient chicks and restored to normal by supplements of vitamin K-active materials.

R. A. Morton, *Ph.D., D.Sc., F.R.I.C., F.R.S.*
Was born in 1899 and educated at the University of Liverpool. He was a Lecturer at Liverpool University from 1924 to 1944, working particularly on absorption spectroscopy and vitamins. He became Johnson Professor of Biochemistry in 1944, and a continued interest in the modes of action of naturally occurring substances led to the discovery of the ubiquinones and of a new group of polyisopentenoid alcohols.

Historically the process has interest in that a haemorrhage-producing agent 'Dicoumarol' isolated from spoiled (mouldy) clover hay turned out to be a natural antagonist of vitamin K. It lowered the concentration of prothrombin, and its action could be reversed by vitamin K. The idea of specific antagonism has powerfully stimulated research into the competitive inhibition of enzyme-catalysed reactions.

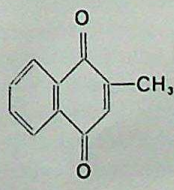
Vitamin K occurs in green leaves in small and variable amounts. As it can be conveniently and quickly assayed, it was soon isolated from dried lucerne (alfalfa) *M. sativa* and characterized.

Early in the study of vitamin K, it was found that fish meal made putrid by microbial attack gained anti-haemorrhagic activity. (It is a fact that many animals obtain vitamin K from the microflora inhabiting their own alimentary tract.) The vitamin K_2 of fermented fish meal differed from phylloquinone in having a longer and more unsaturated polyisopentenoid side-chain.



Vitamin K_2 menaquinone MK-n

A vitamin K_2 family exists, and each member is a menadione (2-methyl-1,4-naphthoquinone) with a polyprenyl side chain at position 3 which may be $—C_{20}H_{33}$, $—C_{30}H_{49}$, $—C_{35}H_{57}$, $—C_{40}H_{65}$, $—C_{45}H_{73}$ [1]. They are designated menaquinones-n (MK-n), n being the number of $—C_5H_8$ units in the side chain.



Menadione

Phylloquinone, menaquinones, and the parent substance menadione are all effective anti-haemorrhagic agents for chicks. The coagulation process is, however, only one facet of the biochemistry of the naphthoquinones, and the role of vitamin K in it is obscure, although various suggestions have been made [2–4]. It is virtually absent from blood, it does not appear to be present in any blood clotting factor, and it is not known to be a prosthetic group in an enzyme. Much more is known about its part in phosphorylation, and this will be dealt with later in this article.

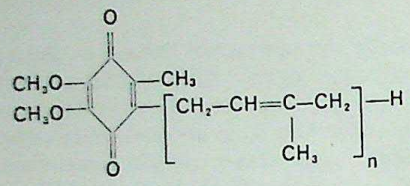
CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Ubiquinones and plastoquinones

Within the last few years, two new classes of quinones (neither falling into the vitamin category) have made a very great impact on some central problems of biology.

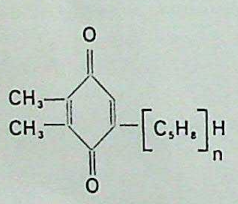
The first family is that of the ubiquinones or co-enzymes Q. They are tetrasubstituted 1,4-benzoquinones having one methyl and two methoxy groups together with a polyisopentenoid side chain:



Ubiquinone Q-n

The individual members of the family differ in respect of the size of the polyisopentenoid chain. In most animals n = 10, so that the polyisopentenoid side chain is $C_{50}H_{81}$, but rats have a mixture of ubiquinones, with Q-9 ($C_{45}H_{73}$) predominating. Many bacteria produce Q-8, and Q-6 and Q-7 occurs in yeasts.

The other new family is that of the plastoquinones. These are trisubstituted benzoquinones, with two methyl substituents and a polyprenyl side-chain. The best known is PQ-9, with a $-C_{45}H_{73}$ side-chain:



Plastoquinone

n = 9, that is $C_{45}H_{73}$ in PQ-9

This was noted by Kofler and then rediscovered by Crane and fully characterized later.

Discovery of ubiquinone

Ubiquinone was discovered at Liverpool [5] and, independently, at Madison, Wisconsin [6]. The background of the two investigations was very different [7].

At Liverpool we had devoted much effort to the study of fat-soluble vitamins, and one of our hopes was that important lipid-soluble substances remained to be discovered. The occurrence of vitamin A stores in animal liver, and of both vitamin A and D in fish liver oils, prompted the investigation of liver as a source of further, quantitatively minor, unsaponifiable constituents. On the other hand, the conversion of β-carotene into vitamin A had been found to occur in the lining of the gut wall, and some fish intestinal oils were exceptionally rich sources of vitamin A. In guinea-pig and other animal species, the lipid obtained from intestinal epithelia was rich in provitamin D (7-dehydrocholesterol). Chromatographic studies of the lipid extracted from horse intestinal mucosae revealed the existence of a new substance characterized by an ultraviolet absorption spectrum with a peak at 270 mμ [8]. The same substance was obtained from the ether extract of an alkali digest of intestinal tissue after chromatography on a column of alumina. The absorption curve shows in addition to the main peak, a well-defined minimum, and inflexions near 320 mμ and 405 mμ (figure 1). The positions on the wavelength scale and the relative intensities constitute a precise chromophoric specification of this new substance SA.

Another investigation, aiming at a closer understanding of the vitamin A deficiency syndrome, included a study of the unsaponifiable matter extracted from the alkali digest of the livers of deficient rats. When this product was fractionated by chromatography on alumina, the '270 mμ' substance (SA) was obtained and separated from cholesterol, and also from a second unidentified substance SC having its own characteristic ultraviolet absorption spectrum [9]. Both 'SA' and 'SC' exhibit a rise in concentration in rat liver showing vitamin A deficiency. The rise in SA proceeds steadily as the rat develops signs of deprivation, but the rise in SC occurs

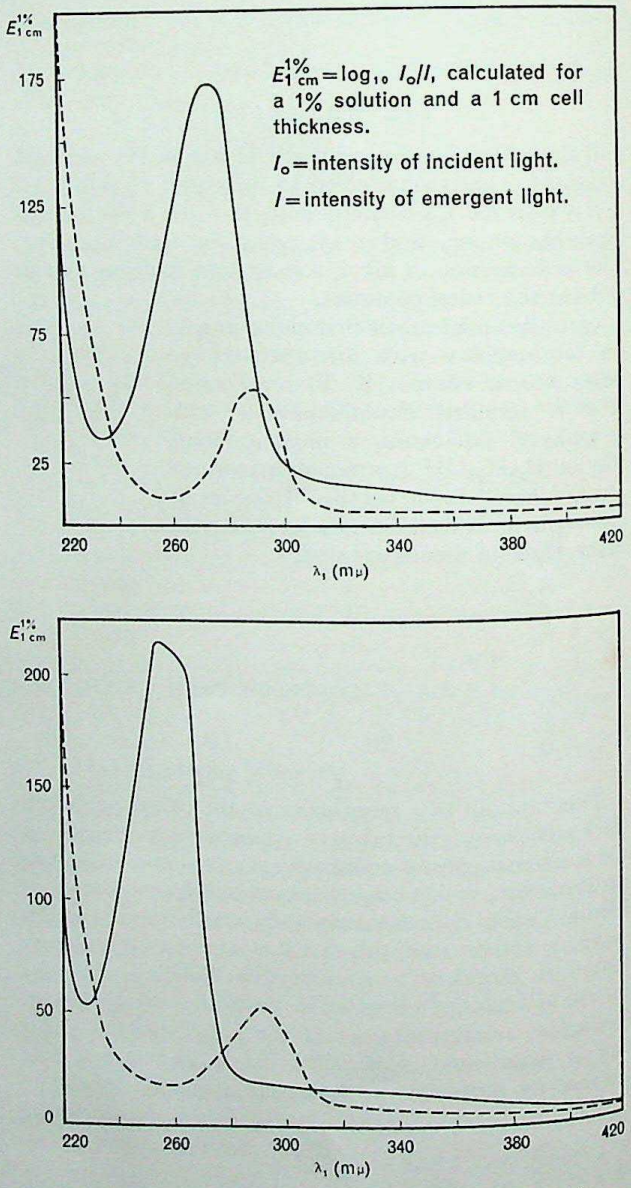


Figure 1 Ultraviolet absorption curves in ethanol. (Above) —— ubiquinone (Q-10) and ----- the corresponding ubiquinol; (below) —— plastoquinone (PQ-9) and ----- the corresponding plastoquinol.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

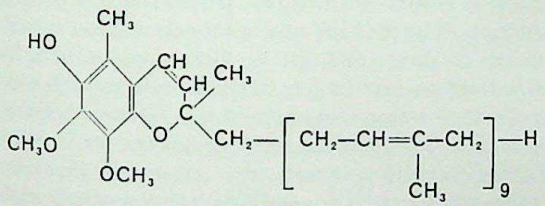
Digitized by Arya Samaj Foundation Chennai and eGangotri

only at a late stage when the animal is losing weight [10].

At about this time a claim was made that vitamin A occurred in yeast. This was unexpected, and a study was made of the constituents of the unsaponifiable matter from baker's yeast. Vitamin A was not observed, but a substance with the same absorption as 'SA' was isolated [11]. It was later shown to be ubiquinone Q-6 [12].

Distribution of ubiquinone and ubichromenol

A further search was made for good sources of SA and SC. The former was obtained from many animal tissues; examples were kidney, liver, spleen, pancreas, lung, heart, sub-maxillary glands, and testes. It was more readily isolated from tissues such as heart muscle and kidney, that were low in such interfering substances as carotenoids and vitamin A, than from liver. The second compound SC was less accessible, and after many trials it was decided that the best available source was 'normal' human kidney. The word 'normal' here means that the kidneys were free from any evidence of disease. The normal kidneys yielded unsaponifiable fractions containing SC; the diseased kidneys had little or none of it. From 43 kg of 'normal' kidneys, obtained over a period by the kind co-operation of pathologists in or near Liverpool, 135 mg of pure SC was obtained. Spectroscopic and other methods led to the constitution, and SA and SC were shown to be isomeric. SA was by then known as ubiquinone, so SC became ubichromenol [13].



Ubichromenol

It is now very easily made from ubiquinone by refluxing the latter with pyridine; the conversion takes place with a good yield. It was natural to wonder whether ubichromenol was an artifact. The evidence for its occurrence as such is substantial, although there is no certain knowledge of its biological role.

Background to coenzyme Q

The work at Madison arose from the study of the respiratory chain, the part of cell metabolism in which substances derived from food are oxidized to give water and the energy-rich compound adenosine triphosphate (ATP). Among the substances resulting *in vivo* from the metabolism of glucose and fatty acids by way of the citric acid cycle, two are of special importance in the present context. The first is succinate, which undergoes enzymic dehydrogenation to fumarate, and the second is the coenzyme, reduced nicotine-adenine dinucleotide ($NADH_2$), which can give the oxidized form NAD and pass on its reducing power by electron transfer. NAD, by accepting H from β-hydroxy-butyrate, α-ketoglutarate, pyruvate, malate, and fatty acids, acts as a bridge. The respiratory chain is made up of a series of carriers along which electrons pass, to react eventually with atmospheric oxygen to form water. In the course of the sequence of electron transfers from succinate, three molecules of ATP are formed for each pair of electrons set free by oxidation. Hence the process as it occurs *in vivo* is called oxidative phosphorylation. When, as often happens with *in vitro* experiments, formation of ATP ceases but oxidation continues, electron transport and phosphorylation are said to be uncoupled.

The process of oxidative phosphorylation is best studied in preparations of intact mitochondria. These organelles are derived from ruptured cells, and D. E. Green's group at Madison were in the forefront in fractionating comminuted heart muscle suspensions by differential high-speed centrifugation. At that time evidence had accumulated that lipid was essential for electron transfer. The possibility arose that in addition to structural lipids, mainly phospholipids forming part of membranes, there might also be lipid-soluble components of the respiratory chain. F. L. Crane and his colleagues studied the material extracted by hydrocarbon solvents from mitochondria [14]. This led them to the discovery of coenzyme Q, which turned out to be the same as ubiquinone. The subsequent chemical work has been described in several reviews. Important contributions to the organic chemistry of the ubiquinones were made by two groups, exploiting skilfully both the classical methods and the newer physical techniques. One was in Basle led by O. Isler [15], and the other at Rahway led by K. Folkers [16]. Isler's elegant work on the isolation and synthesis of vitamins K_2 (particularly menaquinones MK-6 and MK-7) preceded his relatively large-scale isolation of Q-6 from yeast and Q-10 from animal tissue. This made available sufficient material for full characterization of the ubiquinones and their derivatives. Folkers's group also isolated very pure products and similarly performed convincing degradations and syntheses. The availability of solanesol, a nonaprenyl alcohol from tobacco, allowed Q-9 and Q-10 to be synthesized.

Electron transport and cytochromes

Much work on electron transport had already been done, and D. Keilin and E. C. Slater had considerably elucidated the cytochrome system [17]. The cytochromes are haemoproteins in which the iron atom is the site of reversible oxidation-reduction. The reduced forms display narrow absorption bands in the visible region of the spectrum, and the different cytochromes have their own haem prosthetic groups which give rise to differing absorption spectra. The cytochromes are partially separable, and one of them, cytochrome c, has been crystallized, but it seems to exist naturally in a more complex lipid-soluble form. Cytochrome a, which may be made up of two compounds, is a complex copper-containing protein. In the form of cytochrome oxidase it is the final catalyst whereby water is formed from atmospheric oxygen. The other cytochromes have redox potentials that fit the way they precede cytochrome oxidase in the electron transfer chain.

Of the other components of the electron transfer chain, the enzyme succinate dehydrogenase has been purified. As obtained from ox heart, it is a flavoprotein with four atoms of iron per molecule of flavin, present as riboflavin phosphate in a nucleotide. A different enzyme, containing another flavin coenzyme, is specific for removing hydrogen from $NADH_2$. The two enzymes may be designated Fp_S and Fp_D (table II). The comminuted heart muscle preparations used by D. Keilin and E. F. Hartree

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Table I
Ubiquinone in mitochondria from different sources

Source	Q-10 μmoles/g protein
Ox heart	3·4
Pig heart	4·0
Pig kidney	1·1
Guinea-pig kidney	1·6
Rat liver	1·7
Pig adrenal	0·5
Arum maculatum (spadix)	1·4
Rhodospirillum rubrum (chromatophores)	36·0

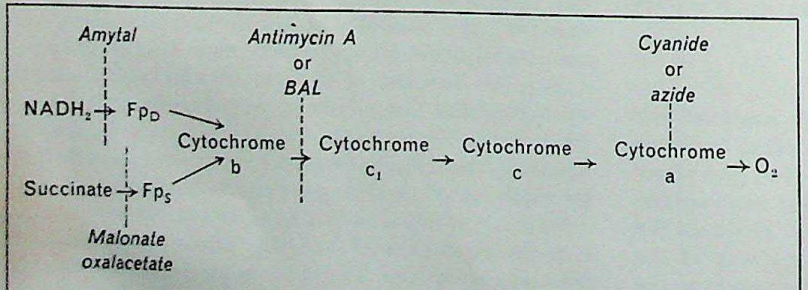
were non-phosphorylating and the mitochondria were damaged or fragmented. Nevertheless, such preparations permitted experiments in which spectroscopic methods used in conjunction with a shrewd exploitation of specific inhibitors led to a rather convincing reaction sequence (figure 2). B. Chance's elegant investigations [18] of the kinetics of reactions occurring in mitochondria tended to confirm the picture.

The functions of ubiquinone and menaquinone

If ubiquinone (coenzyme Q) belongs to the electron transport chain, where is it to be placed? Similarly, if a menaquinone functions in bacterial electron transport, it too must be given its correct place in the sequence, and if a micro-organism has both ubiquinone and menaquinone, a further problem arises.

In order to discuss the roles of quinones in living organisms it is necessary to recall what is known about sub-cellular organelles such as mitochondria, chloroplasts, and the outer segments split off from retinal rods. The mitochondrion is an efficient producer of adenosine triphosphate with the aid of electrons released by oxidation, while the chloroplast produces ATP with the aid of electrons released by radiant energy absorbed by leaf pigments.

The mitochondrion, as revealed by electron microscopy, is sausage-shaped (about $1{\cdot}5 \times 10^{-3}$ mm long and one-third as wide), and a cell may contain several



Inhibition at the cytochrome oxidase site is brought about by carbon monoxide, cyanide, or azide.

Inhibition between cytochrome b and c_1 is effected by 2,3-dimercaptopropanol (*BAL*) and other substances.

Inhibition can occur in phosphorylating preparations before flavoprotein and after $NADH_2$.

Inhibition between succinate and flavoprotein is caused by malonate or oxalacetate.

Figure 2 Electron transport as pictured without quinones.

Table II
Components of the electron transfer chain [23]

Component	Amount present in mitochondria (mμ moles/mg protein)
Flavoprotein of succinate dehydrogenase Fp_S	0·20
Flavin mononucleotide (FMN) (This may measure the amount in nicotine-adenine dinucleotide dehydrogenase Fp_D)	0·15
Flavin, acid-extractable	0·46
Ubiquinone	3·4–4·0
Copper	1·47
Non-haem iron	3·3
Cytochromes:	
b	0·68
c	0·45
c_1	0·21
a	1·31

hundred mitochondria [19]. The organelle has a double lipoprotein membrane enclosing a solution rich in enzymes. The inner membrane has deep infoldings called cristae, extending well into the interior of the mitochondrion. Anchored to the surfaces are particulate aggregates in which the components of the respiratory chain are arrayed. The mitochondrial membrane, four-fifths protein polymer and one-fifth lipid (mainly phosphatide), is sturdy but flexible, permitting swelling and contraction. The half-life of the mitochondrion is said to be about 10 days [20]. D. E. Green and others have prepared various particulate derivatives of mitochondria, some of which retain a capacity for oxidative phosphorylation *in vitro*; in others uncoupling has occurred. Within each mitochondrion there are sub-units capable of oxidative phosphorylation and containing the complete set of enzymes and co-factors. They may be called elementary particles [21] or oxysomes [22].

An attractive theory owing much to Green's group postulates four complexes and a role for ubiquinone as a redox mechanism for shuttling electrons between reduced flavoproteins and the cytochromes [23]. A striking fact about electron transfer particles is their rather constant composition. Compared with the flavoproteins and the cytochromes, the molar concentration of quinone is very high (table 1).

Chloroplasts are disk-shaped organelles ($0{\cdot}5 \times 10^{-5}$ mm in diameter) that occur in green plants, perhaps 50 to a cell. They contain the green chlorophyll pigments and the yellow carotenoids which absorb solar radiation. The photosynthetic process occurs within the chloroplasts in small grana made up of stacks of green disks or ribbons embedded in a colourless stroma. Certain photosynthetic bacteria have particulate chromatophores which also have an organized lamellar structure. A related phenomenon is seen in the stacked disk structure of retinal rod outer segments

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Table III
Occurrence of plastoquinone

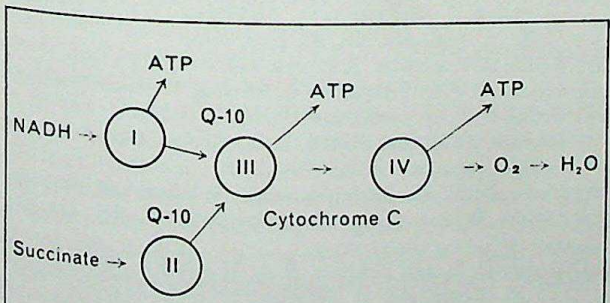
Source	mg/g dry weight
Algae, e.g. *Fucus* species	0·06
Euglena:	
green	1·12
bleached	None found
Photosynthetic bacteria	None found
Leaves:	
Spinach *(Spinacia oleracea)*[1]	0·09
Red beech *(Fagus sylvatico L.* var *cuprea)*	3·0
Maple *(Acer saccharinum L.)*	3·2
Horse chestnut *(Aesculus hippocastanum)*[2]	1·6–3·5
Roots, e.g. Maize *(Zea mays)*	0·019
Tubers, e.g. Potato *(Solanum tuberosum)*	0·001

[1] PQ *B* and PQ *C* are also present in smaller amount together with tocopherol quinones
[2] PQ-4 as well as PQ-9.

bearing the visual pigment rhodopsin. Just as ubiquinone is an integral part of the respiratory chain, so plastoquinone belongs to the photosynthetic phosphorylation sequence.

The evidence for the participation of ubiquinone (Q) includes the following observations: (i) Extraction of mitochondria with a suitable solvent, such as acetone, removes Q, and the ability to oxidize succinate is lost. It can be restored specifically by the addition of small amounts of Q-10 or an isopentenologue. (ii) The ubiquinone in mitochondria can be reduced by substrates such as succinate and re-oxidized by atmospheric oxygen. (iii) Added (exogenous) Q can be reduced enzymically and QH_2 (the quinol) can be oxidized by mitochondrial preparations. (iv) Known inhibitors of electron transport inhibit the oxidation or reduction of Q. Thus amytal blocks the reduction of Q only when the substrate is linked to NAD. Antimycin A inhibits the oxidation of Q whether exogenous or endogenous (figures 2 and 3).

If ubiquinone is correctly placed in the electron transfer chain, there remains the big problem of the manner in which ATP is formed. Hypothetical phosphate transfer mechanisms involving quinones have



I $NADH_2$-Q reductase (contains flavoprotein, Fp_D, and non-haem iron and lipids).
II Succinate-Q reductase (contains flavoprotein, Fp_S, non-haem iron, and perhaps cytochrome b)
III Reduced Q-cytochrome c reductase (contains cytochromes b and c, lipid and non-haem iron).
IV Cytochrome c oxidase (contains cytochrome a, copper, and lipid).

Figure 3 Four-complex scheme for electron transport.

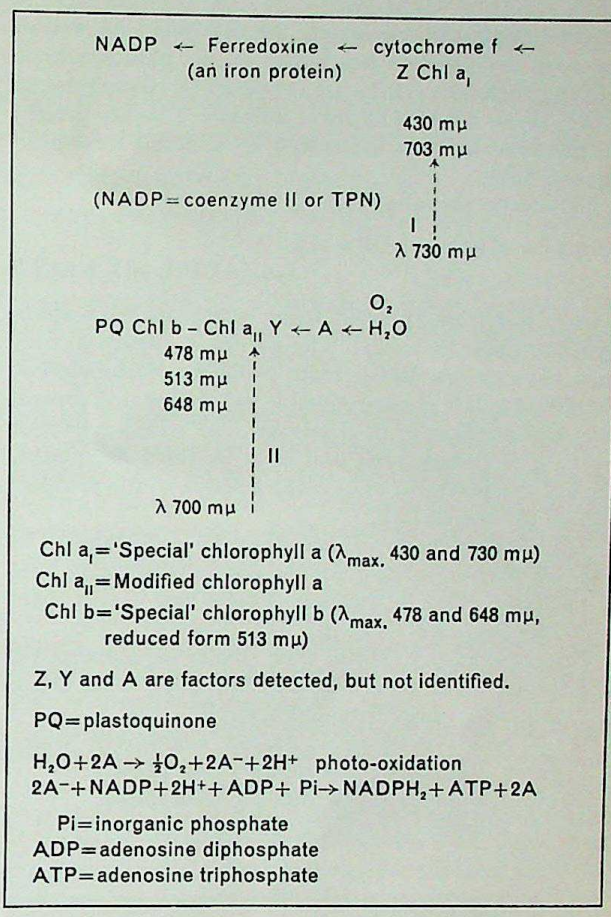

NADP ← Ferredoxine ← cytochrome f ←
(an iron protein) Z Chl a_I
430 mμ
703 mμ
(NADP = coenzyme II or TPN)
I
λ 730 mμ
O_2
PQ Chl b – Chl a_{II} Y ← A ← H_2O
478 mμ
513 mμ
648 mμ
II
λ 700 mμ
Chl a_I = 'Special' chlorophyll a ($\lambda_{max.}$ 430 and 730 mμ)
Chl a_{II} = Modified chlorophyll a
Chl b = 'Special' chlorophyll b ($\lambda_{max.}$ 478 and 648 mμ, reduced form 513 mμ)
Z, Y and A are factors detected, but not identified.
PQ = plastoquinone
$H_2O + 2A \rightarrow \frac{1}{2}O_2 + 2A^- + 2H^+$ photo-oxidation
$2A^- + NADP + 2H^+ + ADP + Pi \rightarrow NADPH_2 + ATP + 2A$
Pi = inorganic phosphate
ADP = adenosine diphosphate
ATP = adenosine triphosphate

Figure 4 Simplified scheme of electron transport in green plants showing two light reactions.

been advanced, but despite a world-wide effort, relatively little indubitable progress in this respect has been made in the last two years or so.

In bacteria, menaquinones are normal to aerobic organisms. In some species, ubiquinone replaces the naphthoquinone, and a few species contain both types—always so far with the same polyprenyl side chain. A. F. Brodie has explored electron transport in micro-organisms [24] and it is clear that the quinone lies between $NADPH_2$ (reduced triphosphopyridine nucleotide) and cytochrome c.

A great deal of work is being done on the production of O_2, $NADPH_2$ (reduced triphosphopyridine nucleotide), and ATP in photosynthesis. The two latter substances are used for carbon dioxide reduction in assimilation. Two photochemical systems SI and SII occur together in the plant, and electrons produced by the former are used by the latter. SI requires absorption of a quantum by a chlorophyll-a complex, and as a result the pigment is oxidized and an unknown substance Z is reduced. SII is a process occurring at a pigment complex which includes chlorophyll-b and chlorophyll-a, and an unknown substance Y is oxidized.

Plastoquinone can be largely removed from chloroplasts by solvent extraction, whereupon photolysis of water (with production of O_2) ceases, but can restart when plastoquinone is returned to the system. Cyclic phosphorylation

$$ADP + Pi \xrightarrow[\text{catalysts}]{} ATP \text{ (overall process)}$$

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

requires plastoquinone among the catalysts [25], and at least one and perhaps two places on the photosynthetic electron transport system are occupied by plastoquinone —or possibly a derived form of quinone. This key process in photosynthesis is illustrated in simplified form in figure 4 [26].

Non-cyclic phosphorylations

$$2NADP + 2H_2O + 2ADP + 2Pi \rightarrow 2NADPH_2 + O_2 + 2ATP$$

involve electron transfer from water to triphosphopyridine nucleotide [27]. The carrier A (figure 4) may be a cytochrome, but is more probably plastoquinone. Ferredoxine is a photo-reducible red conjugated protein very electronegative in character. The whole system of figure 4 is complicated and only partially elucidated. One of the powerful tools being applied to the problem is flash photolysis [28].

The difficulties ahead should not be underrated. The roll-call of chloroplast quinones, any of which may have a catalytic role, is growing. Crane has found eight quinones [29] (see Table III):

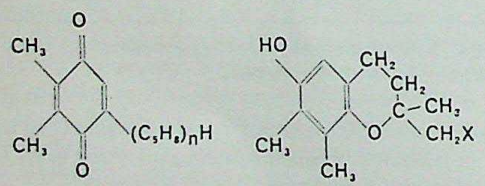
Plastoquinone A (PQ-9) 0·12 μmoles/mg chlorophyll.

Plastoquinones B, C, and D, respectively 0·02, 0·013, and 0·007 μmoles/mg chlorophyll

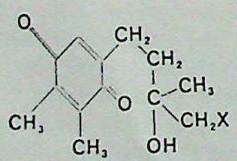
α-, β-, and γ-tocopherolquinones, respectively 0·009, 0·005, and 0·0002 μmoles/mg chlorophyll

Phylloquinone, 0·015 μmoles/mg chlorophyll

Every plastoquinone is a potential precursor of a chromanol



Plastoquinone Chromenol



Tocopherolquinone

each of which could in principle give rise to a tocopherolquinone analogue.

Quinones are peculiarly characteristic of chloroplasts, mitochondria, and bacterial chromatophores. There is evidence [30] that suggests that plastids and mitochondria contain a chromosome controlling their multiplication and development. The organelles contain DNA and RNA and are regarded as self-duplicating. They possess adaptive mechanisms in the sense that chloroplast development is light-responsive, while mitochondria respond to oxygen. If proplastids and promitochondria are distinct precursor organelles, it is significant that in bleached *Euglena* cells green chloroplasts do not develop. Similarly, anaerobically grown yeast contains small promitochondrial structures without cristae and unable to use oxygen. After a few hours of exposure to oxygen, however, they become normal mitochondria and electron transport proceeds. It seems that the biosynthetic processes which are triggered by oxygen include the formation of specific proteins, cytochromes, and quinones. Similarly, light will trigger biosynthetic processes in the chloroplast precursors. A. Gibor and S. Granick base their arguments in part on the study of mutant strains [30]. That organelles exhibit genetic mechanisms and interact with nuclear controlled processes is clearly important.

What goes on in chloroplasts, mitochondria, and chromatophores is thus pretty fundamental. Without the newer quinones, less progress would have been made. With them, some extremely difficult central problems in biochemistry are perhaps seen in better focus.

References

[1] Isler, O., Rüegg, L. H., Chopard-dit-Jean, L. H., Winterstein, A., and Wiss, O. *Chimia*, 12, 69, 1958.

[2] Kopper, P. H. *Nature, Lond.*, 204, 292, 1964.

[3] Olsen, R. E. *Science*, 145, 926, 1964.

[4] Weber, G., Singhal, R. L., and Stamm, N. B. *Ibid.*, 142, 391, 1963.

[5] Lowe, J. S., Morton, R. A., and Harrison, R. G. *Nature, Lond.*, 172, 716, 1953.

[6] Crane, F. L., Hatefi, Y., Lester, R. L., and Widmer, C. *Biochim. biophys. Acta*, 25, 220, 1957.

[7] Morton, R. A. *Nature, Lond.*, 182, 1764, 1958; 19, 1, 1961.

[8] Festenstein, G. N., Heaton, F. W., Lowe, J. S., and Morton, R. A. *Biochem. J.*, 59, 558, 1955.

[9] Heaton, F. W., Lowe, J. S., and Morton, R. A. *Ibid.*, 67, 208, 1957.

[10] Morton, R. A. and Phillips, W. E. J. *Biochem. J.*, 73, 416, 1959.

[11] Heaton, F. W., Lowe, J. S., and Morton, R. A. *J. chem. Soc.*, 4094, 1956.

[12] Gloor, U., Isler, O., Morton, R. A., Rüeg, R., and Wiss, O. *Helv. chim. Acta*, 41, 2357, 1958.

[13] Laidman, D. L., Morton, R. A., Paterson, J. Y. F., and Pennock, J. F. *Biochem. J.*, 74, 541, 1960.

[14] Crane, F. L. *Plant Physiol.*, 34, 546.
Ciba Symposium 'Quinones in Electron Transport', G. E. W. Wolstenholme and C. M. O'Connor (Editors). London. 1961.
Crane, F. L. *Biochemistry*, 1, 510, 1961.

[15] Morton, R. A., Gloor, U., Schindler, O., Wilson, G. M., Chopard-dit-Jean, L. H., Hemming, F. W., Isler, O., Leat, W. M. F., Pennock, J. F., Ruegg, R., Schwieter, U., and Wiss, O. *Helv. chim. Acta*, 41, 343, 1958.

[16] Wolf, D. E., Hoffman, C. H., Trenner, N. R., Arison, B. H., Shunk, C. H., Linn, B. O., McPherson, J. F., and Folkers, K. *J. Amer. chem. Soc.*, 80, 4752, 1958.

[17] Keilin, D. and Slater, E. C. *Brit. med. Bull.*, 9, 89, 1963.

[18] Chance, B. Ciba Symposium on Electron Transport (see [14]).

[19] Green, D. E. *Sci. Amer.*, 210, 63, 1964.

[20] Fletcher, M. S. and Sanadi, D. R. *Biochim. biophys. Acta*, 51, 356, 1961.

[21] Green, D. E., Blau, P. V., and Oda, T. *Science*, 140, 382, 1963.

[22] Chance, B., Lee, C. P., and Estabrook, K. W. *Ibid.*, 140, 379, 1963.

[23] Green, D. E. and Fleischer, S. in 'Horizons in Biochemistry', M. Kasha and B. Pullman (Editors). Academic Press, New York. 1962.
Green, D. E. and Wharton, D. C. *J. biol. Chem.*, 236, 1850, 1961.

[24] Brodie, A. F. *Fed. Proc.*, 20, 995, 1961.

[25] Krogmann, D. W. *Biochem. biophys. Res. Commun.*, 4, 4, 1961.

[26] Wickard, J., Muller, A., and Witt, H. T. *Z. Naturf.*, 18b, 139, 1963.

[27] Arnon, D. I. *Nature, Lond.*, 184, 10, 1959.

[28] Bültemann, V., Rüppel, H., and Witt, H. T. *Ibid.*, 204, 646, 1964.

[29] Henninger, M. D., Dilley, R. A., and Crane, F. L. *Biochem. biophys. Res. Commun.*, 10, 237, 1963.

[30] Gibor, A. and Granick, S. *Science*, 145, 890, 1964.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

The planets

Digitized by Arya Samaj Foundation Chennai and eGangotri

A. Dollfus

It has now become possible that the planets will actually be visited, and this is one of the reasons for the recent increase in interest in them. These studies have necessitated an elaborate international organization, and this article gives a brief description of the organization, as well as an account of the results that have been achieved, including photographs of the individual planets.

The planets of the solar system have naturally always been a subject of curiosity, and the physical study of them is one of the traditional branches of astronomy. Indeed, modern methods of physical astronomy have already made it possible to determine the physical conditions prevailing on their surfaces some properties of their atmospheres, the nature of the surfaces, and even, to some extent, whether there is life upon them. Even so, in comparison with the development of stellar astrophysics, studies of the universe, or even solar physics, the study of the planets remained for long a subsidiary task. However, recent developments in space research have made it possible that they will be directly examined in the near future, and physical studies have become an immediate and urgent preoccupation.

The direct exploration of the Moon and planets has already begun. On 7th October 1959 the Soviet interplanetary station Lunik passed round the Moon and photographed its far hemisphere. On 31st July 1964 the missile Ranger VII hit the Moon after it had transmitted to Earth detailed pictures of the surface; Ranger VIII hit the Moon on 20th February 1965. On 14th December 1962 the Mariner space probe passed sufficiently close to Venus to take radiowave, thermal, and magnetic measurements. Launchings towards Mars have already taken place.

Astronomical observatories have consequently been impelled to increase their planetary studies, and this has led to a remarkable harvest of discoveries. In Europe, high-altitude observing stations such as Pic du Midi (France) have very powerful telescopes for the study, at high resolution, of planetary surfaces; polarimetric studies have been carried out there for many years. In the Soviet Union, the conventional techniques of planetary photometry and spectroscopic studies are well developed, and impressive results have been obtained from radioastronomy and high-powered radar.

In the United States, the planets have been extensively studied with the great reflecting telescopes. Surface temperatures have been measured, and the results combined with those of very detailed spectroscopic studies; radar and radioastronomy are also widely used. Moreover, American astrophysicists are evolving theories of the structure, composition, and motions of planetary atmospheres.

This revival of planetary physics has a number of implications concerning the international organization of astronomical research. It is necessary to co-ordinate researches by international organization and in this paper particular attention will be given to recent discoveries in the study of the planets that have resulted from this kind of collaboration.

A. Dollfus, *Docteur ès Sciences*
Was born in 1924. He works at the observatories of the Pic du Midi and Meudon, France, on a study of the surfaces of the planets and their satellites, and is head of the Department of Planetary Physics at the Observatory of Paris, at Meudon. He has been the President of the Commission of the International Astronomical Union dealing with planets and satellites.

International organization of astronomical research

Since the beginning of this century, the need has been felt to establish an international body to deal with the problems of astronomy. This body is the International Astronomical Union, which belongs in turn to the International Council of Scientific Unions. It consists of Commissions specializing in various fields. Commission 16, in particular, is engaged with the physical study of planets and satellites. This Commission has the task of co-ordinating planetary research on the international scale whenever this appears necessary.

When unusual phenomena are observed in the atmospheres or on the surfaces of the planets, or when particular conditions of illumination allow important observations, it is necessary for many observatories to be able to obtain the necessary data (figure 1). The task of the International Astronomical Union is then to notify observatories possessing particular instruments, and also to collect data for subsequent reduction by the most highly qualified workers and to make them available to the whole scientific community. In case of unpredicted phenomena, observatories are notified either by circulars or by an international telegram system formerly based on the Copenhagen observatory and now on the Smithsonian Institution, United States.

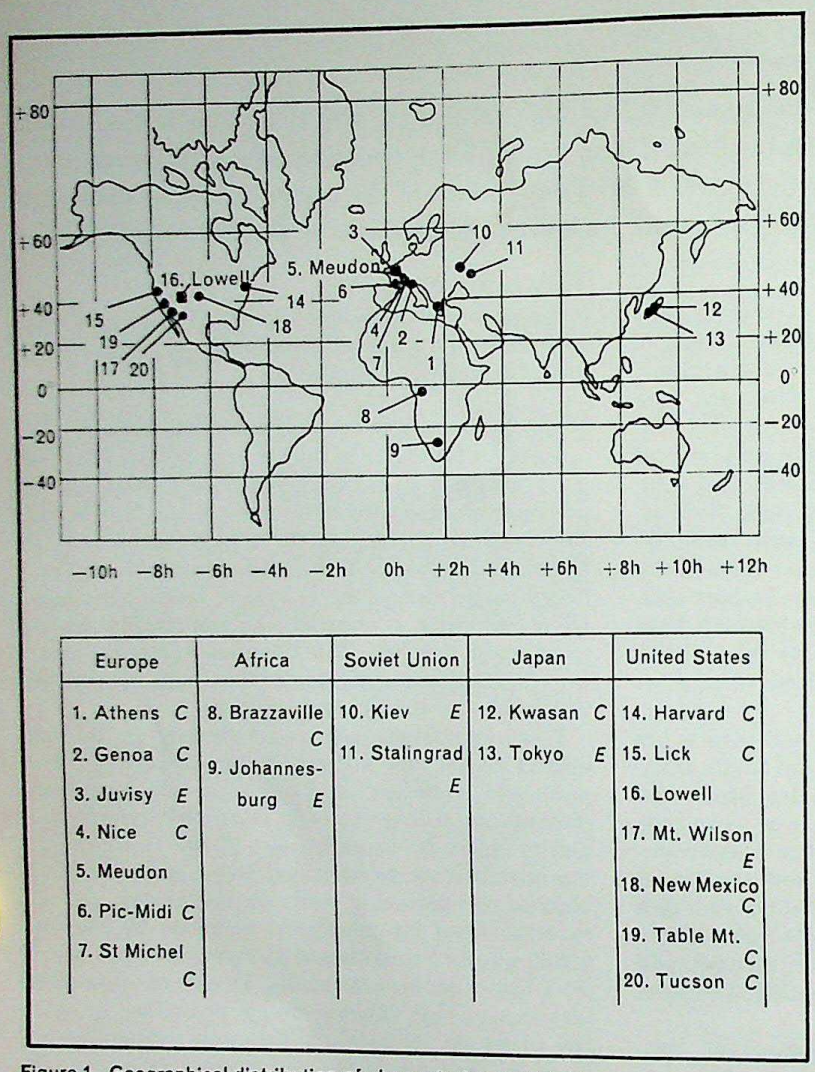
Recent meetings of Commission 16 of the International Astronomical Union at the General Assemblies in Moscow, Berkeley, and Hamburg showed that the development of planetary research would be assisted by the establishment of centres holding photographs of the planets. Considerable collections of photographs of the planets, especially of Mercury, Venus, Mars, Jupiter, and Saturn, had been assembled at various places since the beginning of the century, but the majority were held only at the observatories which took them.

The commission has undertaken the important and very lengthy task of assembling collections of data with the aid of qualified experts. It seems that at least two separate data centres will be necessary in order to meet present needs: one in the United States, and the other in Europe. The establishment of truly international data centres could be effected only by those observatories that were permanent institutions with a long tradition of work in planetary physics, that possessed the necessary qualified staff, and that already held large collections of plates.

In the United States, the Lowell Observatory at Flagstaff, Arizona, established in the last century by the great astronomer Percival Lowell, himself a planetary specialist, responded best to the requirements. The Meudon Observatory in France (the astrophysics department of the

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri



Europe	Africa	Soviet Union	Japan	United States
1. Athens C	8. Brazzaville C	10. Kiev E	12. Kwasan C	14. Harvard C
2. Genoa C	9. Johannesburg E	11. Stalingrad E	13. Tokyo E	15. Lick C
3. Juvisy E				16. Lowell
4. Nice C				17. Mt. Wilson E
5. Meudon				18. New Mexico C
6. Pic-Midi C				19. Table Mt. C
7. St Michel C				20. Tucson C

Figure 1 Geographical distribution of observatories contributing measurements and photographs to the two data centres set up by the International Astronomical Union. Those marked *C* exchange measurements and photographs, those marked *E*, photographs only.

Paris Observatory) was a natural location for the European centre because several thousand photographs of Mars obtained since 1940 at the Pic du Midi Observatory have been catalogued and are available for consultation, and several hundred plates of Jupiter and of Saturn have already been used in many investigations.

The large collections at the Lowell and Meudon observatories are both enriched by photographic material supplied either by other observatories or by individuals (see, for example, figure 7). They include groups of planetary photographs taken in Japan by Professor Miyamoto, series of colour pictures of Mars taken in Johannesburg by Dr Finsen, and the remarkable plates obtained at Mount Wilson by Dr Leighton.

Furthermore, two permanent planetary observing stations have been set up in the United States—one at Table Mountain Observatory (California) and the other at the New Mexico State University, Las Cruces. The regular flow of data from these stations is passed, as is that of the other observatories, to the data centres.

Exchange of data between the Meudon and Lowell centres has been established. The work is restricted only by the high cost of extensive photographic programmes. All information regarding these plates is regularly put on punched cards to facilitate immediate access.

The planets

Venus

Venus is almost exactly the same size as the Earth, and its mean density is only slightly less, 4·9 against 5·52. Venus, however, lies closer to the Sun than does the Earth, the ratio of the distances being 0·72, and in consequence it receives almost exactly twice as much heat. This causes a great dissimilarity in the physical state of the surface, and Venus is a very different world from our own.

Through a telescope, Venus can be seen to exhibit phases, like the Moon. The illuminated crescent is very bright, white with a slightly yellowish tinge, and undifferentiated, with scarcely any spots or characteristic markings. A measurement of the light flux gives the reflecting power of the surface and its variations with phase angle. The fraction of total light reflected, called the 'albedo', is 0·51; this value would be equally well explained by a surface of chalk or a cloud layer. However, polarimetric study of the light, made some years ago by B. Lyot, has resolved the uncertainty: the visible surface is a cloud layer composed of very fine particles of liquid or dust.

Spectroscopic studies, carried out mainly in the United States, have shown a very high content of carbon dioxide, and spectroscopic analysis from balloons and from high-altitude stations by the author has recently indicated the presence of water vapour; these measurements, later confirmed by J. Strong by observations from balloons controlled from the ground, show that the clouds consist of water.

Infra-red or spectroscopic thermal measurements have given the temperature of the atmosphere of Venus at various altitudes. However, very unexpected results have been obtained from measurements of the radio emission from Venus at observatories in the Soviet Union and the United States, supplemented by those from the Mariner space probe when it passed near the planet on 14th December 1962. The very strong emission, increasing with wavelength and decreasing to the limb, seems to indicate a surface temperature as high as 400°C, but unforeseen effects, other than thermal emissions, may be responsible for this result.

The bright crescent of Venus is almost devoid of detail in white light. However, it shows remarkable light and dark patches when photographed in ultra-violet radiation. These transient and continually changing features were discovered by F. Ross at the Mount Wilson Observatory in 1926; they appear to be cloud formations.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

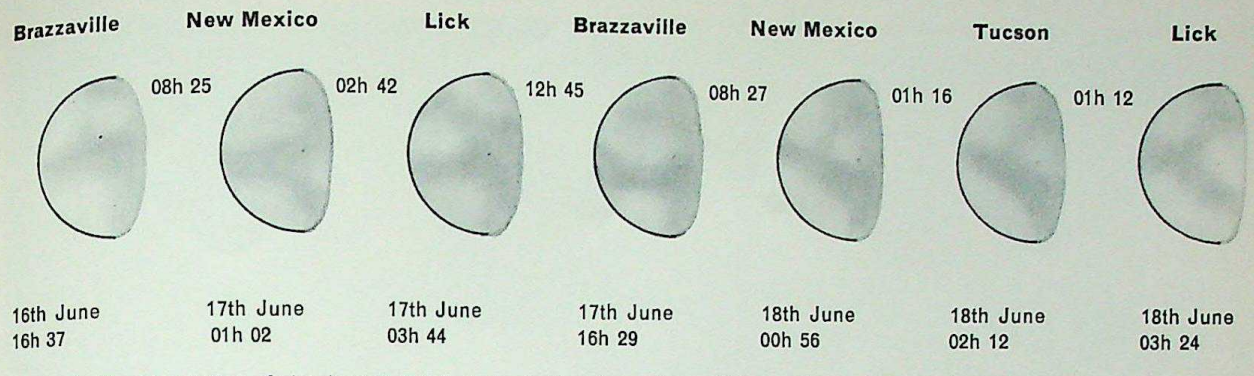


Figure 2 Rapid variation of clouds and dark features in the atmosphere of Venus, from photographs in ultra-violet light taken at intervals of a few hours by means of collaboration between observers in Brazzaville (Congo), New Mexico State University, Lick, and Tucson (U.S.A.). Above: names of observatories and time intervals between pictures. Below: dates and times of observations.

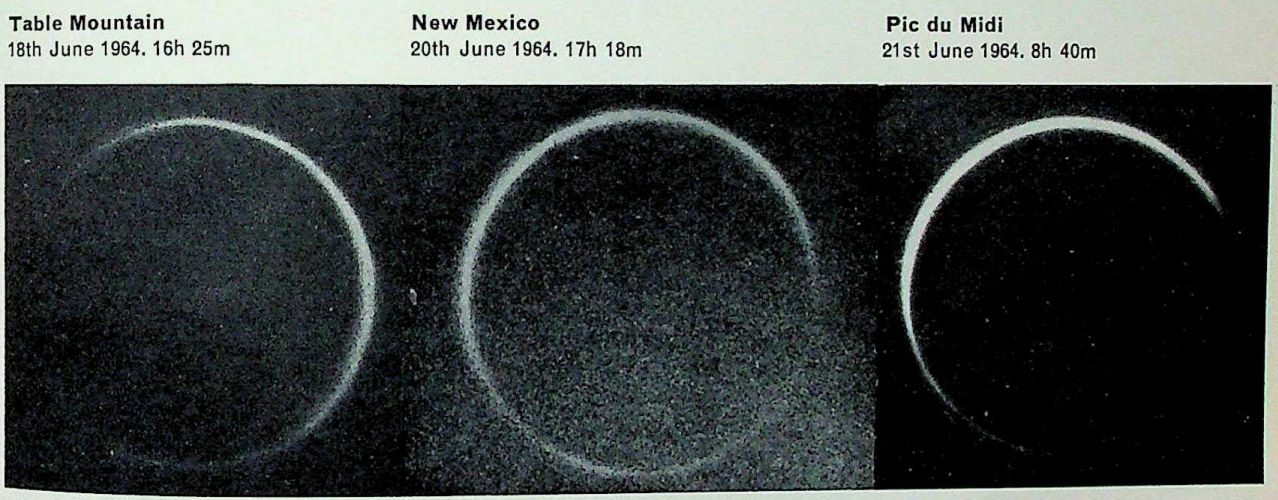


Figure 3 In June 1964 Venus was at an apparent angular distance of 3° south of the Sun. The very narrow crescent was then drawn out into a bright ring, owing to scattering of sunlight by dust in the upper atmosphere of Venus. The whole of the phenomenon was recorded by the observatories of Pic du Midi (France), Table Mountain (California), and New Mexico State University.

One problem in studying the planet is that it is visible for only a short time, at sunset or sunrise, so that any one observer, after taking a series of photographs, has to wait for about 24 hours before taking another series. Meanwhile, the features change so much that they are only rarely recognizable. It is here that international co-operation, which can give a series of pictures at relatively short intervals, becomes extremely valuable.

For example, in 1962, through arrangements made by the International Astronomical Union, a number of observatories took ultra-violet photographs of Venus on each clear evening. The results are still being studied at the Meudon Observatory. The time intervals between pictures were usually only a few hours, and it is possible to recognize features in the atmosphere of Venus, and to examine their rapid variation (figure 2).

In addition, the formation, disappearance, lifetime, and periodicity of large areas of cloud cover can now be studied. Their movement shows the wind speed, which is related to the general circulation of the atmosphere. Their common motion, if confirmed, would be ascribable to the rotation of the planet. Comparative topographic studies, and micrometer and stereoscope measurements of the hundreds of plates received from eight observatories, are now being made.

Other important data have already been obtained through collaboration. On 7th July 1959 there occurred a unique phenomenon, the occultation by Venus of the bright star Regulus. The exact moments of disappearance and reappearance of the star at the limb of the planet, as observed in the Soviet Union and in Europe, gave an exact measurement of the diameter of Venus. The gradual decrease of brightness during occultation is due to the scattering of light by the planet's atmosphere. Observations were co-ordinated by the Harvard College Observatory under the direction of D. H. Menzel and G. de Vaucouleurs; they had been made, or at least attempted, at Madrid (Spain), Le Houga (Gers, France), Merate and Catania (Italy), Beirut (Lebanon), and Bloemfontein (South Africa). The atmospheric pressure gradient and the temperature (about 300°K) were measured at the altitude of about 70 km, where the star's light was almost entirely extinguished in the atmosphere of Venus.

In June 1964, Venus passed through inferior conjunction, that is, it was near the line joining the Earth and the Sun. On 19th June the planet was at only a little over 2° from the Sun and the crescent was so narrow that it seemed a mere arc. A peculiar effect was then observed: the horns of the crescent were elongated as shown in figure 3. The crescent, which should have been a semi-circle, was an almost complete circle. This effect was due

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

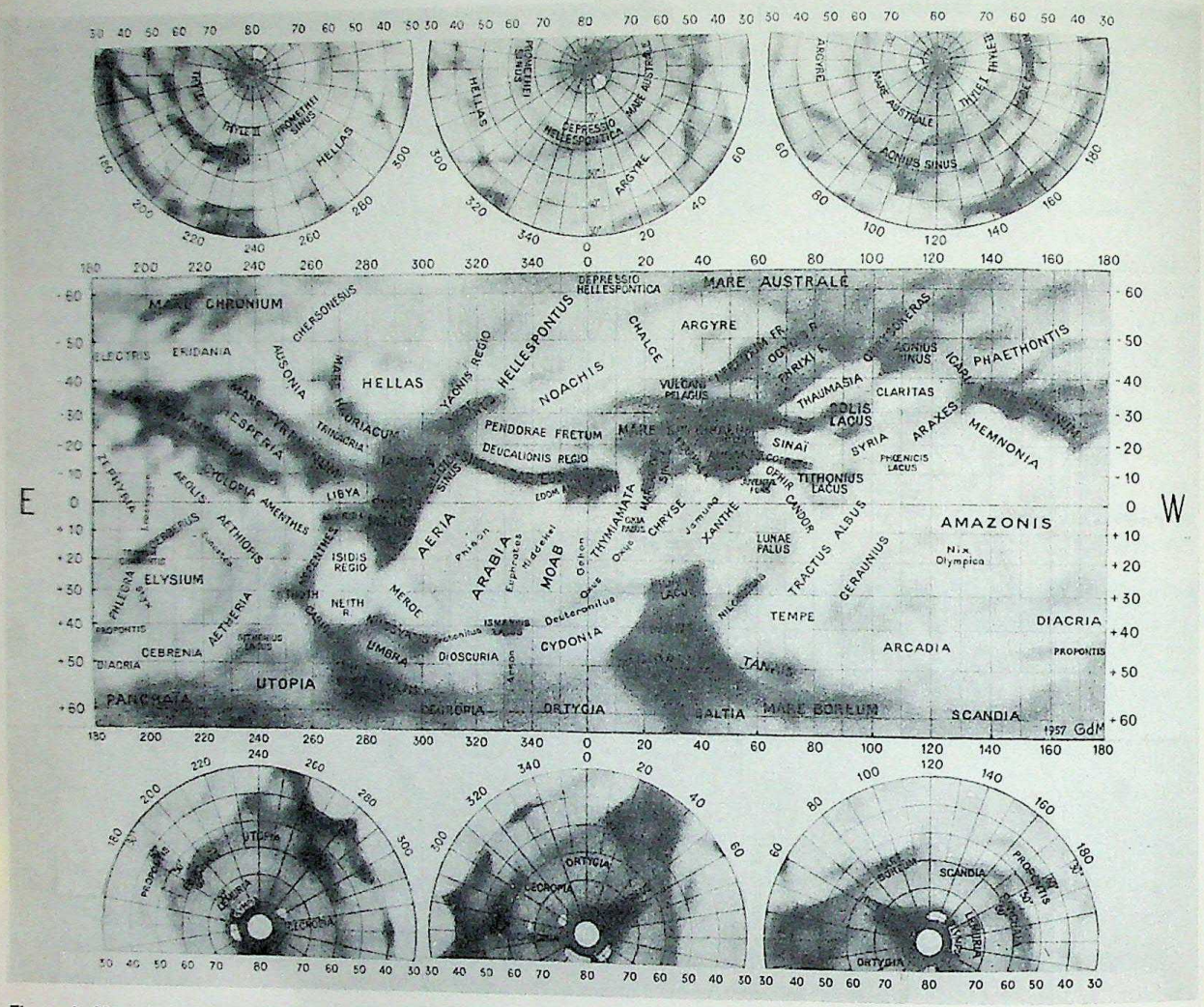


Figure 4 Map showing typical appearance of Mars, from photographs collected at the data centres of the International Astronomical Union, and nomenclature of surface features as adopted by the I.A.U. (Composite map by G. de Mottoni.)

to scattering by very fine dust suspended in the upper atmosphere of Venus, above the ordinary cloud layer. A very thorough study was desirable, and was carried out simultaneously by three observatories, Table Mountain, New Mexico State University, and Pic du Midi.

The accurate measurement of the diameter of this circle gives a particularly accurate value for the diameter of the planet. The very low density of the suspended dust in the stratosphere of Venus was determined; the diameter of the particles is generally less than 2 microns, and their number decreases rapidly upwards above the cloud layer. The atmospheric pressure above the cloud layer is only a small fraction of the air pressure at ground level on the Earth.

Despite much recent work, the data available are still far from adequate to indicate the physical conditions on the surface of Venus. Further studies by conventional astronomical methods, individual or co-operative, are still needed, as well as observations by means of space probes.

Mars

The problems presented by Mars are very different. Our knowledge of this planet is already quite good. Thus, photographic, polarimetric, thermal, and spectrographic studies have shown it to be surrounded by a thin, clear atmosphere having less than one-tenth the density, at the surface, of our own. This atmosphere has a high content of carbon dioxide, probably very little or no oxygen, and enough water vapour to form occasional clouds and seasonal deposits of hoar frost in the polar regions. It sometimes contains fine mists of ice crystals or dust.

The Martian surface is fairly flat and may be covered by a fine powder of iron oxide; its temperature can exceed +15°C at noon in summer, but will fall as low as −50°C, owing to the extreme cooling by night. It is covered with dark patches scattered over the light desert areas (figure 4). These patches vary in shape, appearance, and structure. These changes are mainly seasonal and regular (figure 5), but to some extent irregular and unpredictable. Each Martian year brings about almost the same sequence of events: there is a transient darkening of the polar regions in early spring, which moves at about 35 km per day towards the equator, which is thus reached in a few months. This remarkable behaviour was discovered and described in the last century; astronomers are still undecided as to whether it indicates life on the planet.

Having regard to the wealth of facts already known,

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

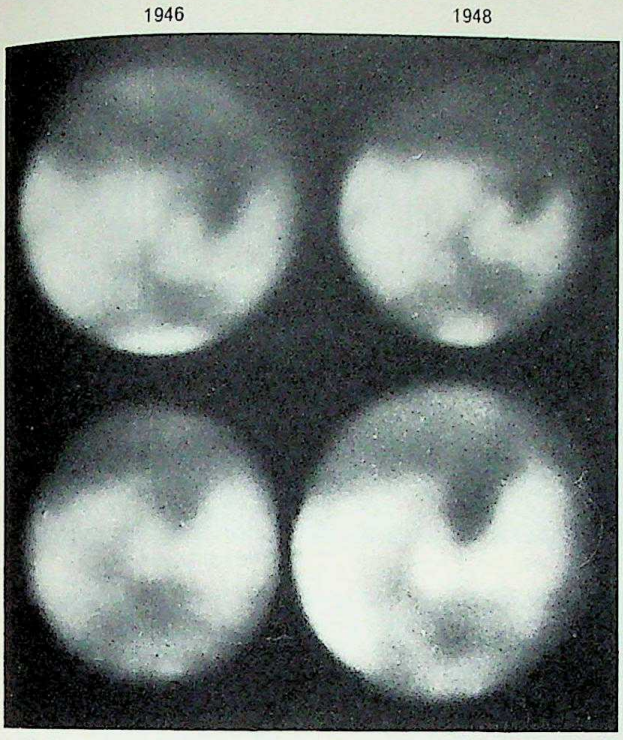


Figure 5 Seasonal variations in position of dark patches on the surface of Mars from 1946 to 1952. The dark triangle with apex downwards is Syrtis Major. (Pictures taken at Pic du Midi by H. Camichel.)

we must restrict this account to some results recently achieved by collaborative observations co-ordinated on a world-wide scale. The planet Mars has one special property. Its period of rotation is 24 h 37 min 22·6 sec, differing from that of the Earth by only 37 min 22·6 sec. In consequence, an observer will see almost exactly the same features as he did at the same time the previous night, Mars having made almost exactly one rotation meanwhile. On successive nights, he still sees almost the same regions. The diametrically opposite regions will not be accessible to him for several weeks. However, by collaboration between observatories at different longitudes, different parts of the planet can be examined at the same time, and this makes a synoptic view of surface features, clouds, and atmospheric mists possible.

For example, the close approach of Mars to the Earth in 1956 was studied by many observatories all over the world. The more recent approaches in 1958, 1960, and 1963, though less favourable, gave rise to similar collaboration, and photographs now assembled by permanent observing stations have permitted an almost complete construction of the appearance of the planet. Physical measurements, such as polarimetric surveys, are also made at various observatories and provide an increasingly accurate knowledge of the cloud cover, its movement and development, and the swirls of dust which momentarily fill the Martian atmosphere. These studies are steadily improving and extending our knowledge of the very individual meteorology of Mars.

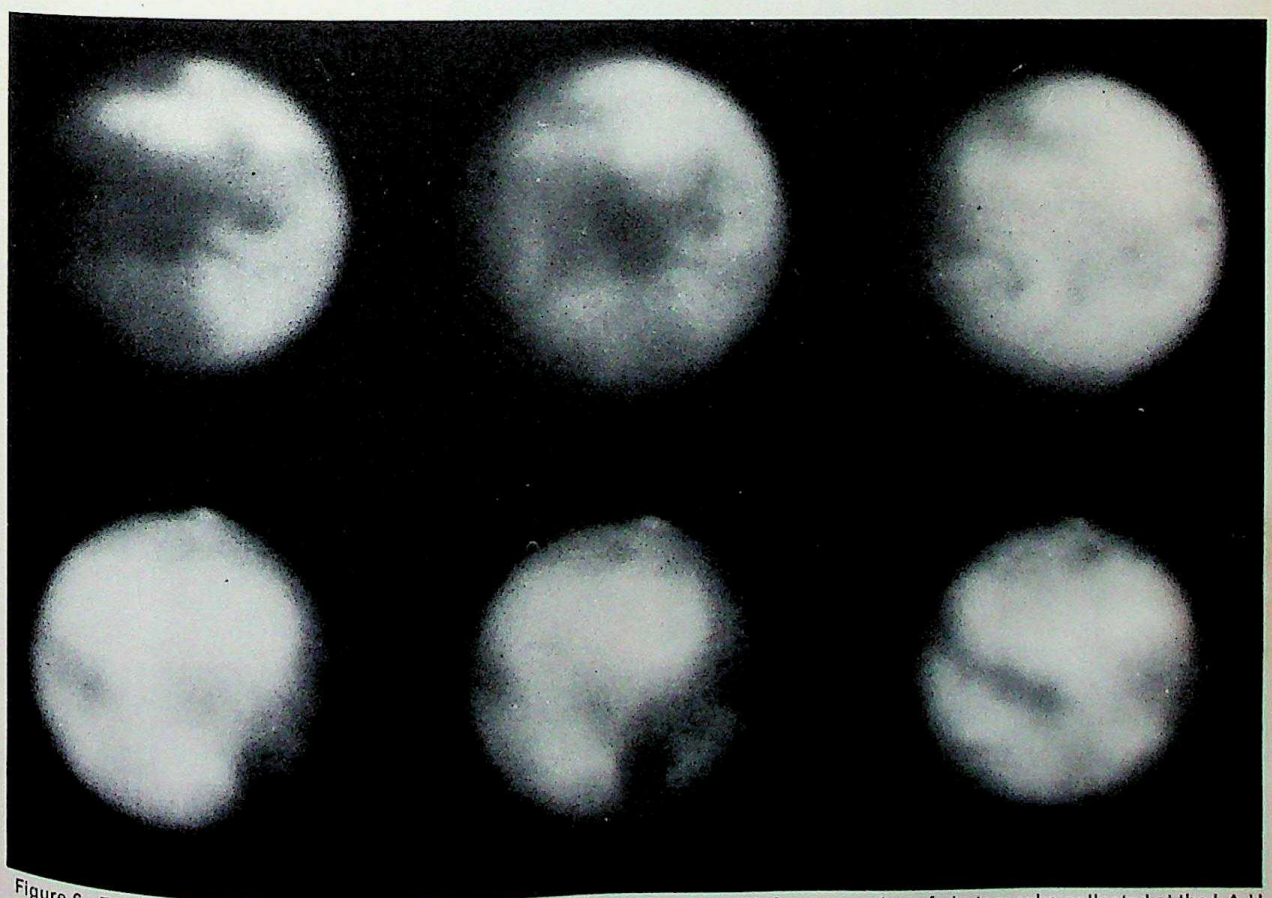
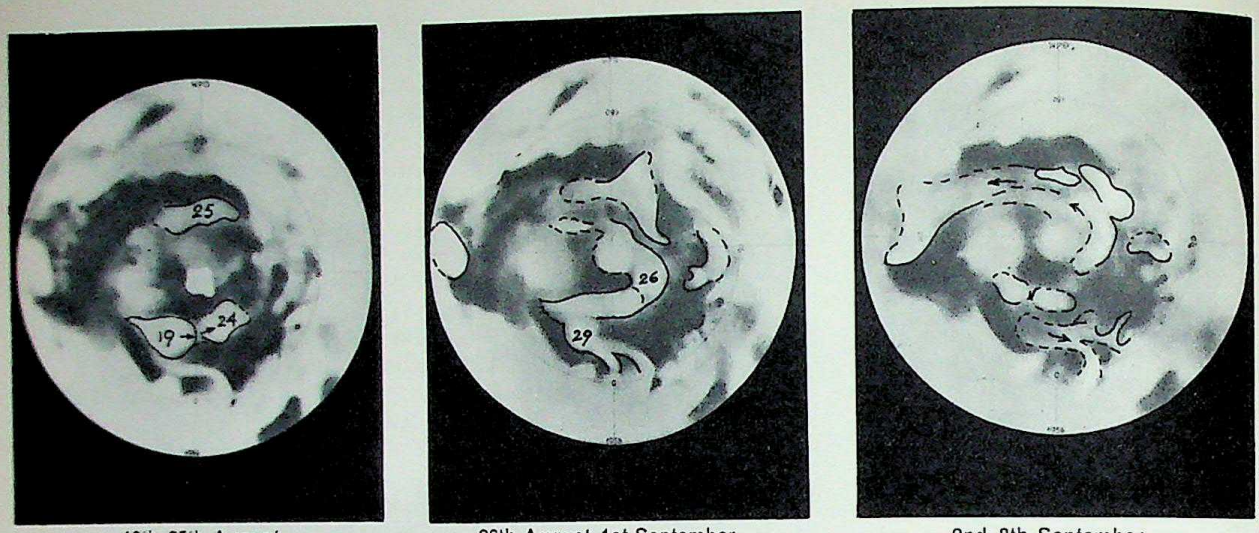


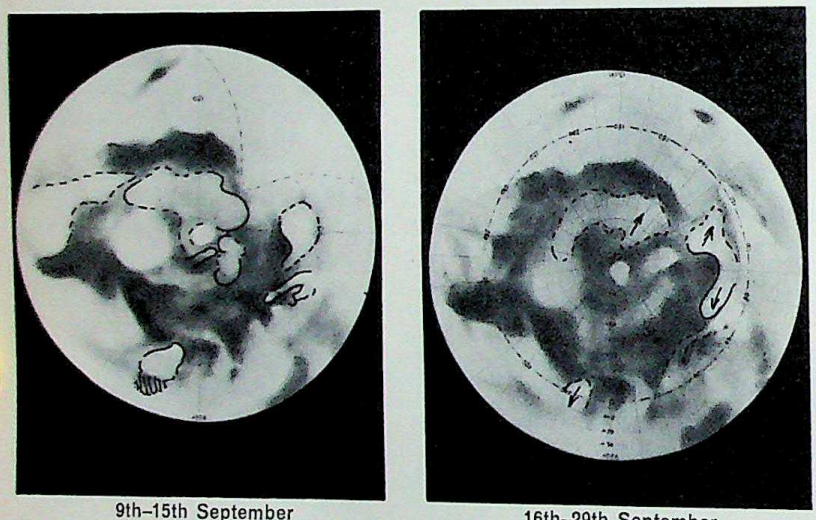
Figure 6 Evolution of fine yellow dust clouds in the atmosphere of Mars in 1956, from a number of photographs collected at the I.A.U. data centre at Meudon.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri



19th–25th August | 26th August–1st September | 2nd–8th September



9th–15th September | 16th–29th September

Figure 7 Development and changes of the dust clouds seen in the atmosphere of Mars during August and September 1956. (Polar co-ordinate maps by G. de Mottoni from about 700 photographs at the I.A.U. Meudon data centre.) Observatories participating: Lick, Lowell, Mount Wilson (U.S.A.); Kwasan, Kyoto (Japan); Volgagrad (U.S.S.R.); Johannesburg, Bloemfontein (South Africa); Athens (Greece); Genoa (Italy); Nice, Pic du Midi (France).

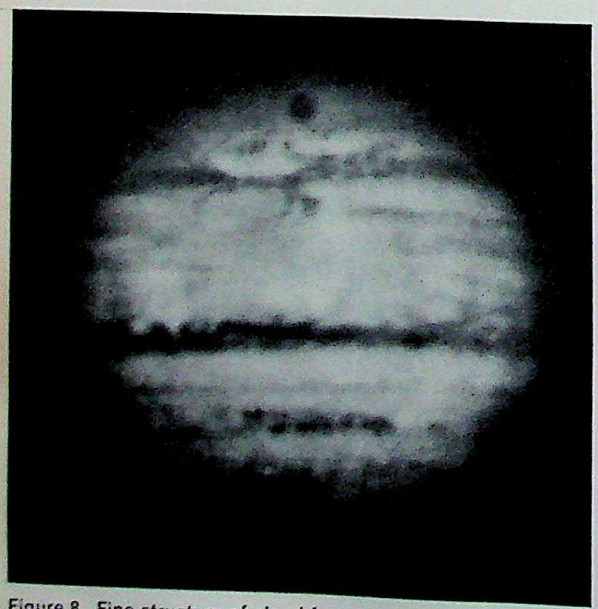
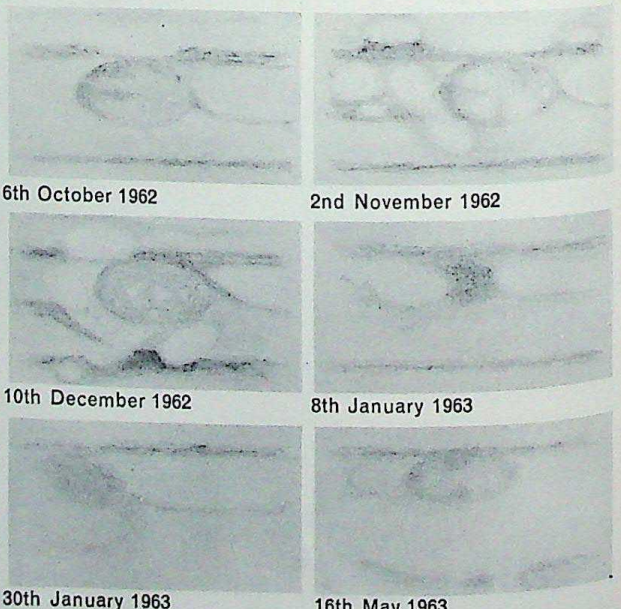


Figure 8 Fine structure of cloud features on Jupiter, photographed by Humason on 23rd October 1952 at the Mount Palomar 200 in telescope. The Red Spot is seen to the left of the central meridian. At the top is the shadow of a satellite.



6th October 1962 | 2nd November 1962

10th December 1962 | 8th January 1963

30th January 1963 | 16th May 1963

Figure 9 Rapid variations near the Red Spot on Jupiter. (J. H. Focas, 63 cm refractor, Athens Observatory.)

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

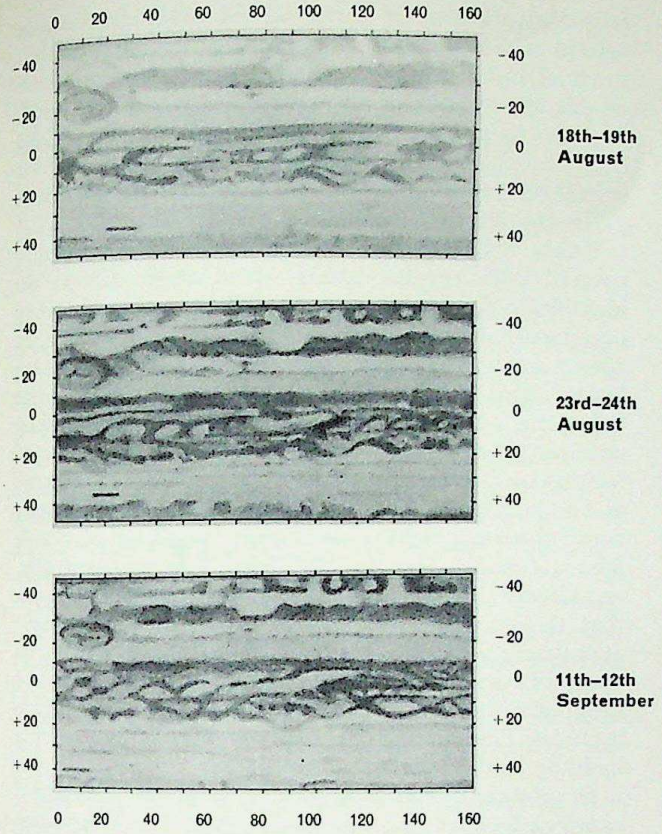


Figure 10 Synoptic map showing evolution of bands and active centres on Jupiter, as in figure 8, for August–September 1962, from pictures taken at Pic du Midi. The Red Spot is at the left. Drawings by M. Marin.

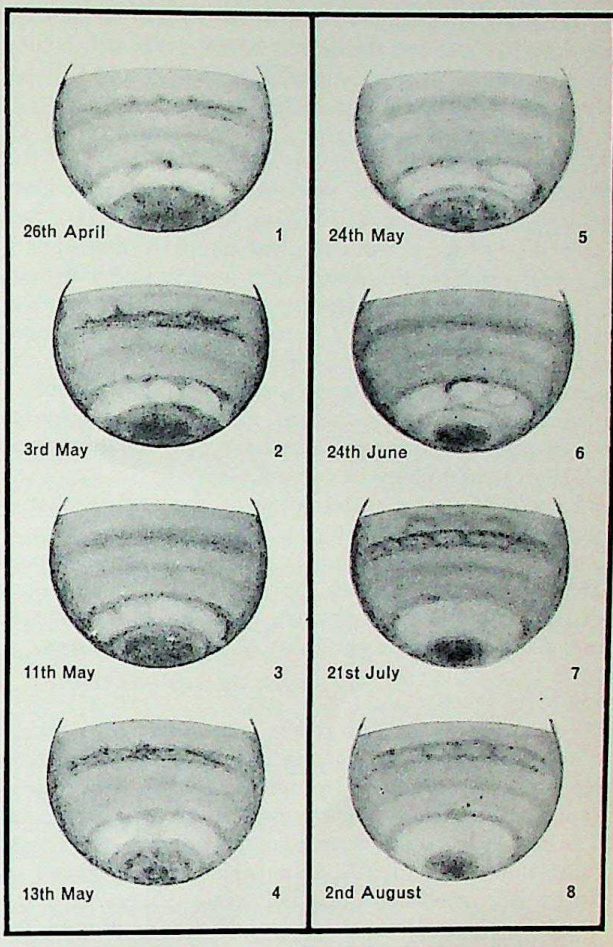


Figure 12 Activity in the northern hemisphere of Saturn, April–August 1960. (J. H. Focas, Athens Observatory)

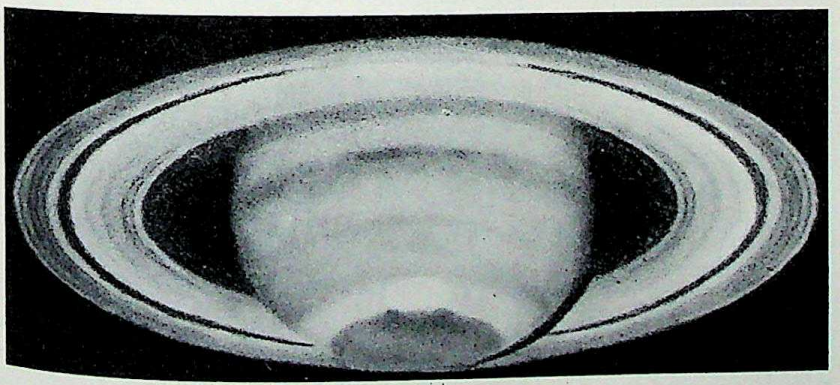


Figure 11 (left) Saturn as seen in the Pic du Midi telescope at magnification 1000 on 26th April 1960, when the white spot visible near the north polar region (north is at the bottom) was discovered by A. Dollfus.

The results of these simultaneous observations are collected at the Meudon observatory in France and at the Lowell observatory in the United States. G. de Mottoni in Italy has studied the results and has been able to make a particularly thorough study of the phenomena accompanying the seasonal variation of the surface patches, which has often been ascribed to the presence of life on the planet. Several thousand plates provided by the data centres enabled him to draw up very detailed maps showing the annual and seasonal variation, and the random variations affecting these surface patches.

The atmosphere of Mars is often filled with clouds of dust (figure 6). De Mottoni used the exceptional dust clouds which formed in the atmosphere of the planet in 1956 to establish maps and data from which the development of these phenomena can be followed in detail (figure 7). This great upheaval of dust in the Martian atmosphere shows motions which can be used to test theories of the circulation of gaseous masses round a planet. The winds on Mars seem to be rarely more than about 35 km per hour, and blow in a regular manner round the dark patches on the surface. There appears to be no turbulence, such as exists in the Earth's atmosphere, but only a regular flow of gaseous masses along paths governed by the topography of the surface. Y. Mintz, at the University of California, has shown that the equations of motion of gas predict this behaviour. The persistence of the dust clouds and their dispersion

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

by diffusion give information as to the size of the dust particles in them and the density of the gas in which they are suspended. The theories of G. P. Kuiper and J. Ryan give an explanation of these effects.

At the Lowell observatory, earlier studies by E. C. Slipher of the scattering or absorbing clouds in the Martian atmosphere as seen in blue light have been greatly extended. A. G. Wilson has discovered many interesting properties of these features of the atmosphere of Mars, which could not have been investigated had it not been for the number of photographs that were available.

The ultimate object of these studies is to determine more accurately the atmospheric pressure on Mars, the physical properties of the gas and of matter suspended in it, and their seasonal variations; and also the movements of gas masses, the seasonal atmospheric circulation, and Martian meteorology in general.

In addition, the examination of the surface should permit a geological analysis of the uppermost layers, a broad assessment of tectonics and erosion, and in particular an elucidation of the reasons for the seasonal variations of the dark patches, a matter of importance to a discussion of the possibility of life on the planet.

Jupiter and Saturn

We can describe in this article only some of the results obtained from studies of these planets. The atmosphere of Jupiter contains very numerous opaque clouds, probably consisting of crystals of frozen ammonia. The planet has a diameter 11·2 times that of the Earth, and rotates very rapidly, in a period of only about 10 hours. The resulting Coriolis forces are large, and the atmospheric circulation is governed by laws which can be deduced from hydrodynamic investigations. The clouds of ammonia which form parallel bands in the atmosphere contain very rapid eddies and local variations, and friction is also involved (figure 8).

For many years, the British Astronomical Association in London has co-ordinated visual observations by participating observatories. Drawings, micrometry, and measurements of the time at which the moving clouds pass across the imaginary line called the 'central meridian' have demonstrated peculiar effects such as the great currents perpendicular to the axis of rotation, and the irregular movements of the 'Red Spot' and the currents around it (figures 9 and 10). These movements are very rapid, but they are accompanied by slow and progressive variations which are still not well understood. Several hundred plates, some of them from as long ago as 1888, were studied by J. H. Focas, who found slow periodic variations in the stratified band distribution typical of these clouds. Thus the very complex mechanisms of turbulence and convection in the atmosphere of this planet have in part already been ascertained. In order to give a clearer demonstration of rapid and complicated effects, it now seems to be necessary for several observatories to carry out regular and continuous cinematography of the planet.

Unlike that of Jupiter, the disk of Saturn is usually covered with regular bands which show almost no identifiable features (figure 11). There are only very occasional exceptions to this uniformity. For instance, in 1960 a small bright spot was unexpectedly observed on Saturn. This transient white elliptical object, in latitude 50° north, was accompanied by several others; as they were carried along by the planet's rotation, these unusual features made it possible to determine the rate of rotation of the cloud layers in the atmosphere, as a result of very many observations from seven stations located in South Africa, Canada, the United States, France, Australia, and Greece (figure 12). This collaboration had the result that the equatorial regions of the planet's extensive atmosphere were shown to contain an extremely rapid eastward current, over 1400 km per hour faster than the mean rate of motion of the atmospheric layers in medium latitudes. This strange phenomenon has still to receive a hydrodynamic explanation.

In 1966 the famous ring of Saturn will be illuminated exactly edgeways for a few days, and at about the same time the Earth will pass through the plane of the ring. These conditions should make it possible to determine the size of the particles forming the ring.

Bibliography

Flammarion, C. 'L'Astronomie Populaire'. Editions Flammarion, Paris. 1955.

Bruhat, G. and Schatzman, E. 'Les Planètes'. Presses Universitaires de France, Paris. 1952.

Kuiper, G. P. 'The Atmospheres of the Earth and Planets'. University of Chicago Press, Chicago. 1950.

Idem. 'The Solar System', Vol. III. 'Planets and Satellites'. University of Chicago Press, Chicago. 1961.

Slipher, E. C. 'The Brighter Planets'. Lowell Observatory, Flagstaff, Arizona. 1964.

Antoniadi, E. M. 'La Planète Mars'. Librairie Hermann, Paris. 1930.

de Vaucouleurs, G. 'Physics of the Planet Mars'. Faber and Faber, London. 1954.

Peek, B. E. 'The Planet Jupiter'. Faber and Faber, London. 1958.

Alexander, A. F. 'The Planet Saturn'. Faber and Faber, London. 1962.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

The surface fauna of the ocean

P. M. David

The immediate surface layers of the sea are potentially of great economic and ecological importance—many fish spend part of their life there. However, very little is known of these layers despite their accessibility. This article describes some of the animals that are found there, which include the only known oceanic insect species and a range of plankton of an unusual blue colour.

It is curious that very little is known of the flora and fauna of the immediate surface layers of the sea, although they are easily accessible parts of the environment and can be studied with relatively unsophisticated apparatus. These layers are of particular interest because the physical and chemical conditions of the environment are liable to greater and more rapid changes than occur elsewhere in the open seas. In addition, organisms living there are exposed to the full daylight spectrum, while those in deeper layers receive only a spectrum from which large portions have been absorbed by the water.

Yet it is in only the last ten years or so that oceanographers have begun to make a systematic study of surface organisms, and it is possible at present to give no more than a description of some of the animals found at the surface, as nothing is known of their physiology and little of their ecological relationships.

The larger and more visible elements of this population have been known to seafaring people for centuries. These include such animals as *Physalia*, the 'Portuguese man o' war' (figure 5), *Velella*, the 'by the wind sailor' (figure 4), *Ianthina*, 'the purple storm snail' (figure 1), and *Glaucus* (figure 6), which Sir Alister Hardy suggests may have been the animals referred to in Coleridge's 'Ancient Mariner':

> 'Yea, slimy things did crawl with legs
> Upon the slimy sea'.

Little was known of the smaller fauna, and although the blue crustacea characteristic of the surface layers occurred from time to time in small numbers in tow nets, they were thought to be uncommon. This lacuna in our knowlege of the sea may be attributed in a large part to the use of the conventional tow net. This is a conical bag of fine netting attached to a metal ring and is usually fished from the stern of a vessel under way. It is necessary to tow it on a very short line to keep such a net at the surface, and if it is worked from the stern of a ship it will tow in the disturbed turbulent water of the wake. If a longer rope is used, the weight of the net ring will take the net below the surface. Nets used in this way catch the plankton that is common in the upper part of the whole zone in which green plants can live, and give little indication of a specialized surface fauna.

Methods of study

Because the sea surface is so accessible, simple apparatus such as buckets, grapnels, and various sorts of hand or dip nets suffices for a great deal of collecting. Presumably Columbus's sailors used the simplest of gear to make the first recorded catch of Sargasso weed. But even fine-meshed hand-nets miss a lot, and it has been necessary to devise modified plankton nets to take standard samples of the smaller animals. Clearly it is necessary to have a net which will fish away from the ship's wake and other disturbances caused by the passage of the ship through the water. This has been achieved in two ways—firstly by paying out the net from a drifting ship and then hauling it in at a standard speed, and secondly by fishing a net from a boom projecting from the ship's side while the ship is under way.

The first method has been used by Russian workers [1–6], who have also fished surface nets from an anchored ship in a current. The surface net described by R. P. Willis [7] is designed to fish at very slow speed and may be set on a very long line to avoid ship disturbance, although this is not explained in the paper which describes it. Yu. P. Zaitsev [6] has experimented with a variety of nets of various shapes supported by floats and has used a multistage net consisting of five nets, each sampling a layer 10 cm thick, on a ladder-like frame. Some of the nets used from a drifting ship have been as large as 3 m across the mouth, though this must restrict their use to fairly calm conditions.

The second method, that of fishing alongside a ship using a boom or spar projecting from the ship, has a longer history. The earliest record I can find of its use is in William Beebe's book 'Galapagos, World's End' [8]. The net appears to be an ordinary ring plankton net, but seems to have been towed at high speed. A one-metre net fished at high speed from a boom was used by the *Discovery* Expedition in the early 1930s to sample shoals of *Euphausia superba* in the Antarctic. It was very successful, but it was only occasionally used. A. E. Parr [9] devised and fished a special sampler towed from a boom for catching Sargasso weed. The net could be fished at speeds up to 10 knots, but as it was made of coarse mesh netting it did not catch small plankton organisms.

In 1962 the National Institute of Oceanography began trials with a variety of surface sampling devices which led to the building of a net mounted between two surf boards that skimmed along the sea surface (figure 2).

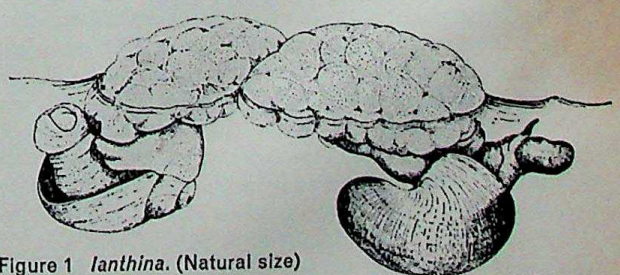


Figure 1 *Ianthina*. (Natural size)

P. M. David, *M.A.*
Was born in Carmarthenshire in 1924 and educated at Sherborne School and Worcester College, Oxford. He has worked at the National Institute of Oceanography, Wormley, Surrey, since 1949. He served aboard R.R.S. *Discovery* II in the Southern Ocean 1950–51, and frequently on short trips in the North Atlantic between 1952 and 1962, and aboard R.R.S. *Discovery* on the International Indian Ocean Expedition in 1963 and 1964. His main interests are oceanic zoology, plankton life histories, the fauna of the surface of the sea, and photography of planktonic animals.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

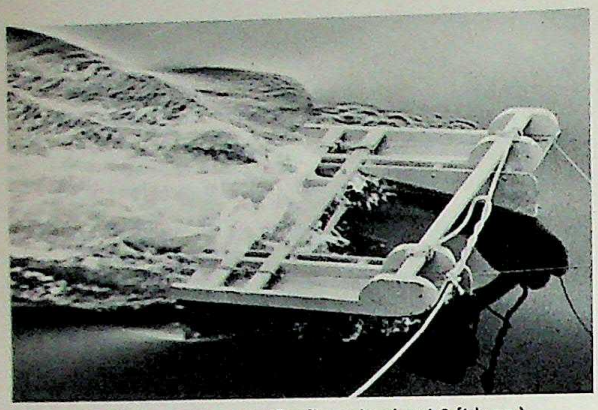


Figure 2 The neuston net. (Surfboards about 6 ft long.)

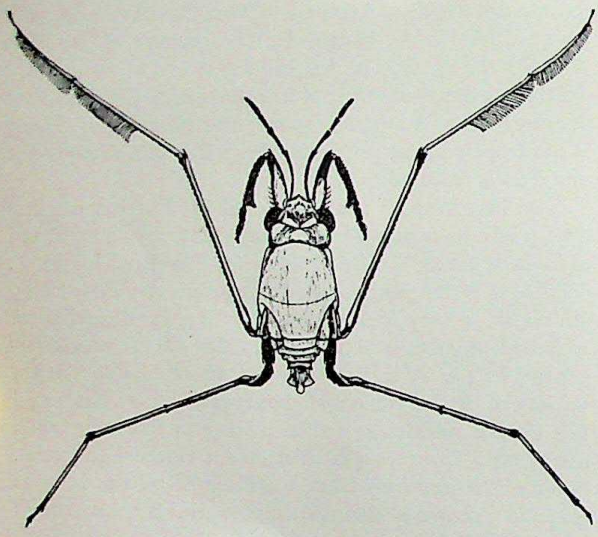


Figure 3 *Halobates.* (Body length 4 mm)

Two keels were incorporated in the design, so that by varying the length of one of the towing bridles relative to the other the net could be made to sheer away from the ship's side. Although the net was designed to be towed at 8 knots, it has been used at 5–6 knots because the animals in the catch are found to be less damaged at these slower speeds. The sheer of the net due to the effect of the keels was not sufficient to take the net clear of the bow wave on R.R.S. *Discovery*, and so a twelve-foot boom was used as a towing point. The net has operated in winds up to force 9. In these winds it jumps rather erratically on the waves, but it still seems to take adequate samples.

The animals of the surface layers

In considering the surface fauna, one has to differentiate between the transient fauna whose presence is the result of vertical migration, and the permanent fauna that remains in the surface layers at all times. The transient fauna includes large animals such as *Tuna*, the dolphin fish *Coryphaena*, and other large pelagic fish which are only sampled in their larval and small postlarval stages, but the transient plankton seems to be adequately sampled by small fast-moving nets. Catches of surface plankton often show a very marked tendency to patchiness, so much so that some hauls consist almost entirely of a single species. In general, however, the species taken

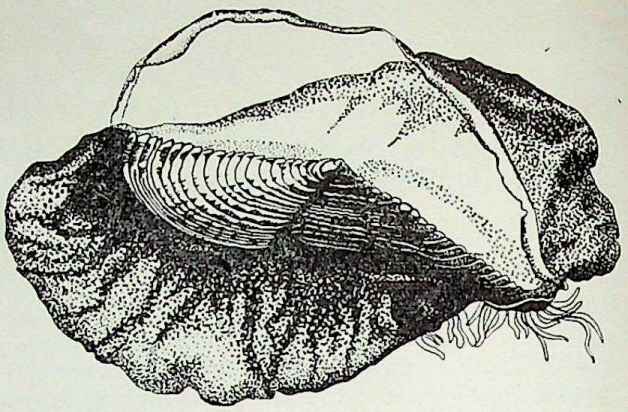


Figure 4 *Velella.* (Length, 4 cm)

at night are predominantly those caught in more conventional nets at various depths, though the numbers of fish larvae, for example, seem often very high compared with samples from below the surface. It may be possible to explain this by assuming that, below the surface layer, the animals are dispersed to a greater or lesser extent in depth, whereas when they migrate upwards, they concentrate in a narrow layer at the surface boundary.

The permanent surface fauna, apart from the large animals, such as cetacea, turtles, and sea snakes, may be divided into two main components. There are, firstly, those animals which are adapted entirely to a surface existence, partly in air and partly in water, which A. I. Savilov [1] has called the Pleuston, and secondly those animals, the Hyponeuston, which inhabit the immediatly subsurface layers. In addition to these main components, there are two minor categories. One of these is the Epineuston—animals that live entirely on the surface; the various insect species of *Halobates* (figure 3) are the sole representatives of these. The other is the life associated with flotsam, which does not seem to have been given a collective name.

Pleuston

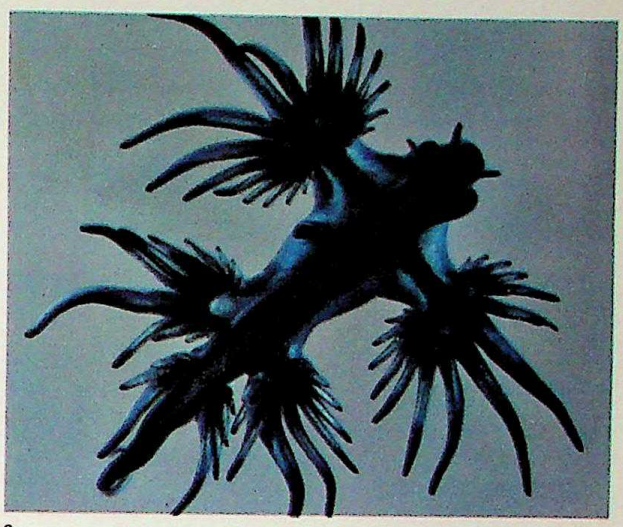
Pleustonic animals are usually characterized by the possession of some sort of float. *Physalia* (figure 5), for example, has a large and elaborate float which has been described by A. K. Totton [10]. In the same paper is an account of the behaviour of this most conspicuous pleustonic animal. *Velella* (figure 4) also has a float, but the float, unlike that of *Physalia*, is chitinous and continues to float after the rest of the animal has died and rotted away or been eaten. The 'empty' floats are of considerable importance in the ecology of surface animals, as they form a substrate for egg laying by animals such as the mollusc *Fiona* [11] and the water strider *Halobates*, and they offer settlement to barnacle larvae, and perhaps to early larvae of the gastropod mollusc *Ianthina* (figure 1).

Porpita (figures 7, 8) is related to *Velella* and also has a float of hard material. It differs from *Velella* in that the float is a disk with numerous air chambers that looks like a cross section of a tree stem. The floats continue to drift about at the surface after the death of the animal and are frequently seen with a variety of sessile animal growths on them. *Porpita* is much more restricted in its distribution than *Velella* or *Physalia*, as it is found exclusively in tropical waters, whereas the others may also be found in temperate regions.

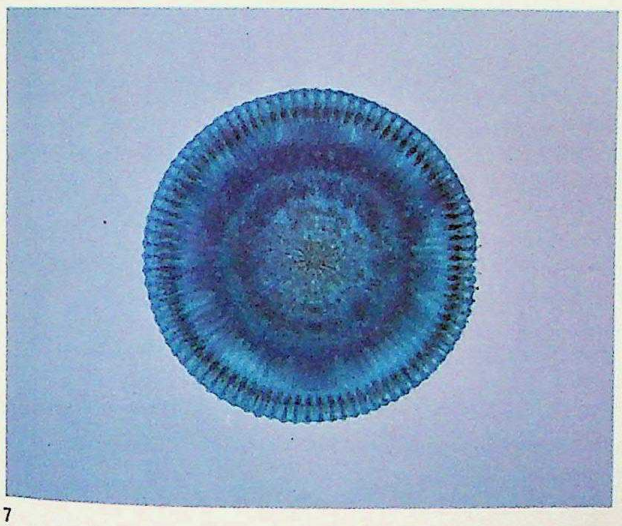
CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

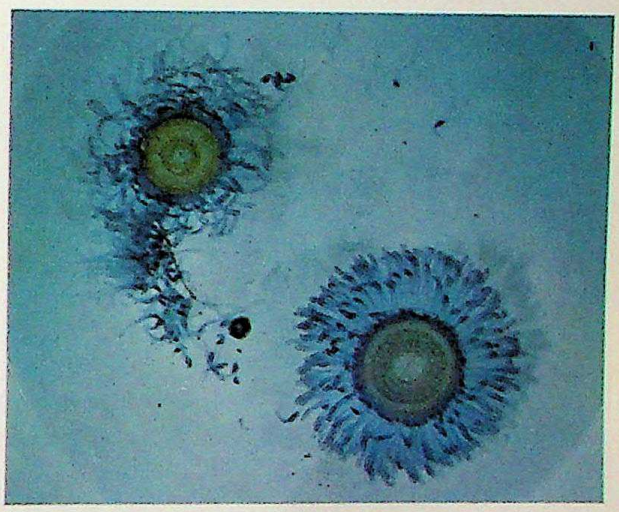
5



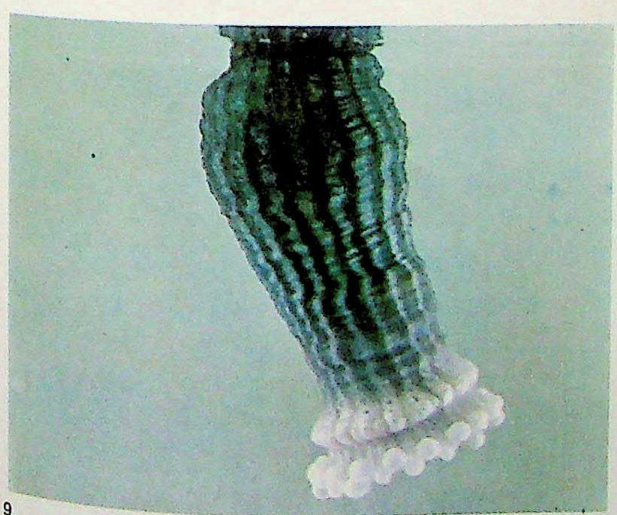
6



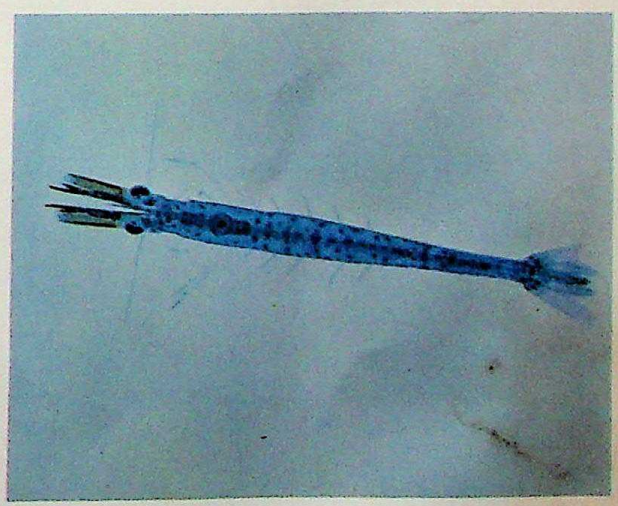
7



8



9



10

Figure 5 *Physalia.* A very young example of the familiar Portuguese man o' war, 6 mm in length.

Figure 6 *Glaucus.* A nudibranch mollusc from tropical waters, about 3 cm long.

Figure 7 *Porpita.* A very young example of a tropical surface living siphonophore, 3·5 mm in diameter.

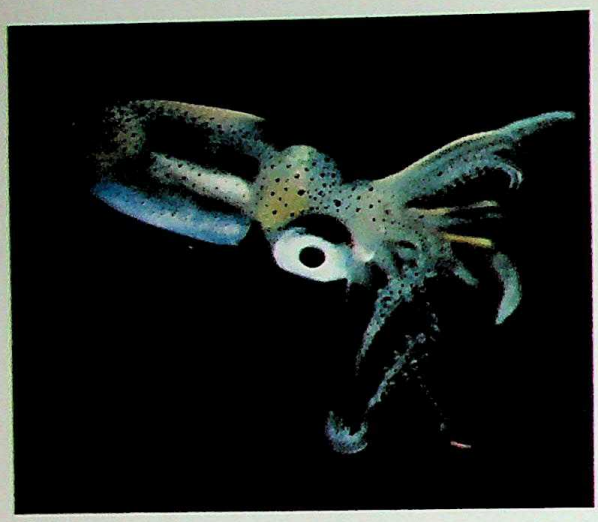
Figure 8 *Porpita.* Two specimens of a tropical surface-living siphonophore. The float of the larger specimen is 3 cm in diameter.

Figure 9 An Abylid anemone. A pleustonic coelenterate 2 cm long.

Figure 10 *Parapeneus longipes.* A strongly pigmented blue hyponeustonic decapod, about 3 cm long.

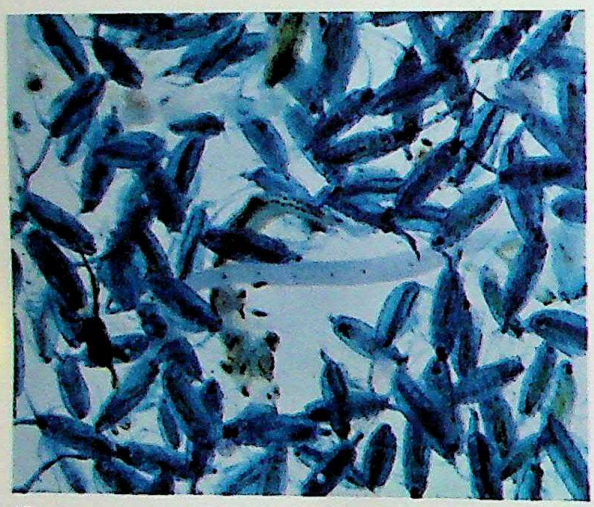
CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

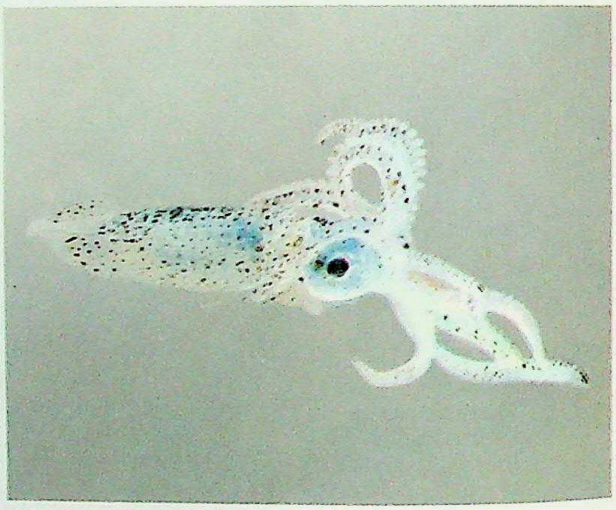


11

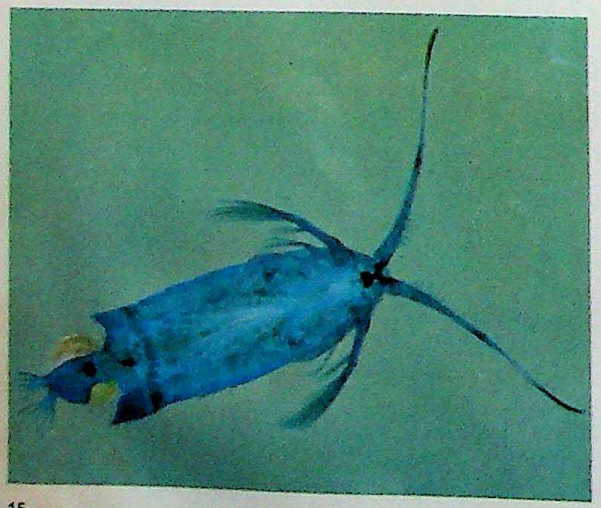
12



13



14



15

16

Figure 11 *Teleoteuthis.* A hyponeustonic squid with blue interference colours, 2·5 cm in length.

Figure 12 *Halobates* eggs on floating 'turtle grass'. (×7)

Figure 13 Pontellid copepods and fish larvae from a daytime neuston net haul. (×5)

Figure 14 A faintly blue pigmented squid 2 cm long.

Figure 15 *Pontella scutifer.* A hyponeustonic copepod, about 3 mm long

Figure 16 *Argonauta*, about 4 cm long.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Ianthina and the allied genus *Reclusia* are gastropod molluscs that entrap air with part of the foot, coat the bubble so formed with a slimy secretion which becomes tough on exposure to air, and construct floats from a number of bubbles stuck together. The process has been photographed and described by D. P. Wilson [12]. If *Ianthina* loses its float, it sinks and is unable to make another.

Free-floating anemones of the family *Abylidae* (figure 9) are found in tropical waters. They are quite distinct from the anemones that are frequently found on flotsam, although they can assume a sedentary existence on occasions. The float is a small, tough collection of bubbles in the centre of the foot and is retained at one side of the foot when the animal is attached to a substratum. These anemones may be blue or dull green in colour. They occur in the Indo-Pacific region, but have not been recorded from the Atlantic.

Stalked barnacles also make a float of bubbles on occasions, but the bubbles usually surround a nucleus of some floating fragment, such as a small *Velella* float, a piece of wood, or a lump of fuel oil. It is not known how the animal makes its float.

The nudibranch mollusc *Glaucus* is a common pleustonic animal in warm waters. It is very buoyant and apparently contains bubbles of gas within the body cavity; it has been described as 'crawling on the underside of the surface film', but my colleague on R.R.S. *Discovery*, M. V. Angel, informed me that the body breaks the surface, though the finger-like processes do not. I have never seen any signs of crawling or swimming among the specimens I have looked at. The animals float in an anatomically upside-down position with the ventral surface towards the sky. They do not appear ever to crawl on flotsam, and release their eggs in strings of about 12 to 15 straight into the sea, unlike most other nudibranchs, which lay eggs on a substratum.

Epineuston

The only epineustonic animals are five species of *Halobates*, which are the only insects which live in the open ocean. They are water striders (figure 3) and seem to live entirely on the top of the surface film and are, when alive, very buoyant if pushed beneath the surface. The buoyancy is due to air trapped in the hairs on the body, and preserved specimens sink after the hair has become thoroughly wet. It has been reported that *Halobates* submerges itself at times, but I think this is unlikely. Its eggs (figure 12) are laid on a variety of floating debris, such as birds' feathers, seaweed, and even fuel oil. It seems possible that they may feed on small animals trapped in the surface film; they are themselves eaten by small fish [13].

The hyponeuston

Among the permanent members of the hyponeuston may be found representatives of most of the main planktonic groups. Larvae of all sorts are common, and in some areas, notably in the Black Sea, fish eggs and young fish larvae are most abundant [5]. Though in the open parts of tropical oceans the biomass of hyponeuston may not be large, large amounts of hyponeuston may be caught in the more fertile inshore waters and in those parts of temperate regions that have been investigated.

Perhaps the most striking characteristic of the permanent hyponeustonic organisms, at least in oceanic water, is the intense blue colour of so many of them, which is quite different from the colour of the plankton in general. This blue colour is strongly developed in species of copepods, particularly among the Pontellidae (figures 13 and 15), decapod crustacea (figure 10), medusae, fish, and squid, and it is faintly developed in salps, in some squid (figure 14), and in some decapod crustacean larvae.

In some of these animals, the colour is due to pigments, and in others to interference effects. Thus pontellid copepods and one or two species of decapod crustacea possess a pigment which has been extracted and examined spectroscopically [14]. It is probably a protein-linked carotenoid and has an absorption peak at 640 mμ. Further investigations are in progress to determine the pigments in *Physalia*, *Velella*, *Porpita*, and a number of the less strongly pigmented hyponeustonic animals. However, in many fish and in an undescribed species of squid (figure 11), the blue colour is the result of interference effects; species of the copepod genus *Sapphirina* are also coloured in the same way.

The function of this widespread blue coloration is not known. It could be in part due to one particular group of strongly pigmented animals, such as the Pontellid copepods, being a key food organism for a number of other animals. More probably it is a form of adaptive coloration that affords some concealment in the brilliantly lit blue of the upper layers.

Perhaps one of the most interesting examples of adaptive coloration found in hyponeustonic animals has been recorded by Yu. P. Zaitsev [5]. He observed that if the small fish *Mugil auratus* were caught in a sea on which waves had produced specks of foam, the fish had silver-white backs; after they had been in a small tank for about six minutes, the usual green-blue tinge returned. He also noted that larvae of the anchovy and the sprat remained transparent until they were 30–35 mm long, as did some other larvae, while the larvae of red mullet and rockling are dark blue and silver. All these thus have colours in marked contrast to those of the adults.

Apart from its coloration, the hyponeuston as a whole shows little sign of adaptive characteristics which might be special to the environment. Copepods of the Pontellidae (figure 13) are capable of jumping out of the water for distances of up to about six inches, and this may be a special escape mechanism, although it might also be the result of the normal escape reaction when performed near the surface. However, this is unlikely.

The paper nautilus *Argonauta* (figure 16), a rather uncommonly caught hyponeustonic animal, has a curious habit of riding on the upper surface of the bells of the *Scyphomedusae* and has been observed on *Pelagia* and *Rhizostoma*; indeed, it is always worth hand-netting these quite common medusae to see if they have *Argonauta* on them. There does not seem to be any explanation of this habit known at present.

A specimen of a surface living fish (*Mupus* sp.) was observed in an aquarium to feed preferentially on small animals trapped by surface tension in the surface film—it 'rose' to these like a trout feeding on the imagos of Ephemerids, and would even eat dried plankton providing it floated. There may well be other animals utilizing this rather special food supply.

Fauna associated with flotsam

Although flotsam is not generally common in the oceans,

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

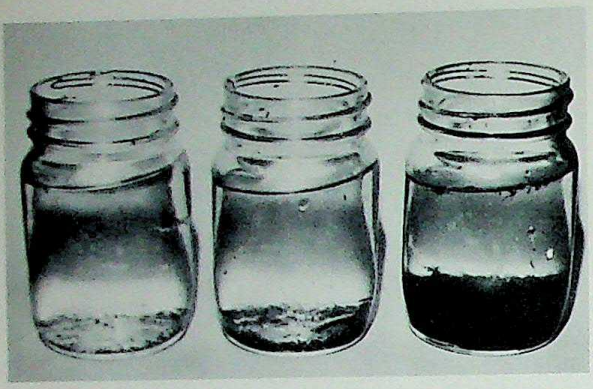


Figure 17 Blue plankton; catches made with a three-stage neuston net by day. From left to right: Catches from (1) 8–12 in, (2) 4–8 in, (3) 0–4 in.

it is often locally concentrated by convergences and surface water movements. Almost anything which floats in the sea becomes covered with an epifauna and very soon acquires an attendant company of animals ranging in size from large fish like *Coryphaena* to small crustacea. William Beebe has given an account of the accumulation of life in a sharp boundary zone in the Pacific [13], and several members of the *Kon Tiki* expedition described the animal community associated with their raft.

Electric light bulbs, planks, logs, fishermen's floats, boxes, and fuel oil are some of the objects which become inhabited, and they may often be almost unrecognizably obscured by barnacles, hydroids, anemones, and other sessile forms, while amidst this living substrate, crustacea, nudibranchs, polychaete worms, fish, and crabs can be found. Japanese fishermen have recognized for many years the fact that large pelagic fish are often associated with floating logs [15] and can deduce the presence of floating objects from the distribution of the various species of fish in the vicinity. They even make rafts to attract the fish. The reasons for the association are not understood. The fishermen have suggested that the shade given by a floating object and the presence of small fish which could act as food for the larger ones are the attracting factors, but S. Kojima [16] considers that neither explanation was wholly satisfactory.

Floating seaweed buoyed up by bladders may be encountered in all the oceans. The unique circulation in the Atlantic makes the weed accumulate in a large area, and it has a permanent existence in the Sargasso Sea. In this sea, the weed propagates itself by vegetative means and the old heavily encrusted parts break off and sink. There have been many observations made on the weed and its fauna from the time of Columbus to the present day, but although Parr [9] made a quantitative study of the weed there seems to have been little or no quantitative work on the fauna. K. Uchida and Y. Shojima [17] have studied the larval and juvenile fish accompanying drifting weed, and have devised a method of collecting clumps of weed which could lend itself well to quantitative studies, yet this remains to be done. The biomass of floating weed and its accompanying fauna is, however, very small in comparison with the biomass of the free-living neuston. Most of the animals associated with floating weed show adaptations of colour and form suitable to the habitat, but nearly all of them are littoral, not oceanic animals. In the Sargasso Sea, however, one crab, *Planes minutus*, appears to be indigenous to the floating weed and is specially modified [18].

Future work

While investigations into the fauna of the surface layers are at a very preliminary stage, investigations into the flora have hardly begun at all, and few investigations into the hydrology of the surface layers have been made. The surface layers contain many eggs and larvae of fish and invertebrates, and they also contain many forms which are rarely if ever caught in other layers. A programme of investigation designed to study the surface ecosystem will yield results of both economic and zoological interest. Surface sampling gear is simple to use and compared to other oceanographic apparatus is cheap—it is possible to use a neuston net from almost any ship that can go slowly enough.

The surface layers are exposed to much more light than the deeper layers, and the animals have to endure both ultra-violet and to a lesser extent infra-red radiation; the turbulence is often great, and changes in temperature and salinity must be more extreme there. Physiological investigations into the adaptations to this environment would be most interesting, but the animals have not so far proved any more tractable to living in captivity than those from greater depths.

There are certain questions which need to be answered about the surface fauna as soon as possible—how thick are the layers which it inhabits (figure 17); how stable are these layers in varying sea states; and to what extent is the permanent surface fauna ecologically involved with the transient fauna, and vice versa.

Many hyponeuston animals are herbivorous, and there must be a permanent flora in the surface layers in spite of the very high light intensities. Whether this flora will prove to be very specialized and able to photosynthesize in light intensities which are normally inhibiting in the sea [19], or whether photosynthesis takes place only at times when the light intensity is low remains to be seen. There are clearly a number of problems to be solved.

Acknowledgments

I am much indebted to Dr Vera Fretter for permission to use figure 1, which is reproduced from the Ray Society Monograph on British Mollusca, and to Miss Nancy Naftel for drawing figures 3 and 4 from photographs of the live animals.

References

[1] Savilov, A. I. *Dokl. Akad. Nauk SSSR*, 110, 3, 1956.
[2] *Idem. Ibid.*, 122, 6, 1958.
[3] Zaitsev, Yu. P. *Zool. Zh.*, 38, 9, 1959.
[4] *Idem. Nauk Zap. Odess. Biol. Stants.*, 2, 1960.
[5] *Idem. Zool. Zh.*, 40, 6, 1961.
[6] *Idem. Vopr. Ekol.*, 4, 1962.
[7] Willis, R. P. *N.Z. Jl sci.*, 6, 1963.
[8] Beebe, W. 'Galapagos, Worlds End'. Putnam, London. 1924.
[9] Parr, A. E. *Bull. Bingham oceanogr. Coll.*, 6, 7, 1939.
[10] Totton, A. K. '*Discovery*' *Rep.*, 30, 1960.
[11] Bayer, F. M. *Bull. mar. Sci. Gulf Caribb.*, 13, 3, 1963.
[12] Wilson, D. P. and Wilson, M.A. *J. Mar. biol. Ass. U.K.*, 35, 1956.
[13] Beebe, W. 'The Arcturus Adventure'. Putnam, London. 1926.
[14] Herring, P. J. *Nature, Lond.* 205, 1965.
[15] Yabe, H. and Mori, T. *Bull. Jap. Soc. sci. Fish*, 16, 2, 1950.
[16] Kojima, S. *Idem.*, 21, 10, 1956.
[17] Uchida, K. and Shojima, Y. *Idem.*, 24, 667, 1958.
[18] Beebe, W. 'Nonsuch, Land of Water'. Putnam, London. 1932.
[19] Steeman-Nielsen, E. *Physiol. Plant.*, 5, 1952.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Development of the theory of the flotation of sulphide ores

M. G. Fleming and J. A. Kitchener

Although the froth flotation process is of enormous importance in world economy, it was developed in the past largely by empirical methods. Now modern experimental techniques are being used to investigate the mechanism of action of the surface-active substances employed; this article describes some of the results obtained, particularly on the flotation of galena with xanthates.

Judged by the scale on which it is operated—approaching 10^9 tons of ore treated per annum—the froth flotation process for concentrating valuable minerals is one of the most impressive technical applications of surface chemistry. It depends basically on rendering selected constituents of an ore floatable, but from this simple concept has developed a sophisticated technique that is both versatile in scope and sensitive in discrimination. Selectivity is achieved by the use of several types of chemical reagent. The most essential, known as 'collectors', are surface-active compounds which render a mineral hydrophobic—that is, induce a finite angle of contact. 'Activators' may be added to enhance the activity of collectors; 'depressants' are used to inhibit flotation of unwanted minerals. Finally, 'frothers' are added to generate a transient foam to carry the floated mineral over the lip of the cell. By judicious control of these reagents and of pH, a series of consecutive separations can be affected economically on an ore as complex as that shown in figure 1 and of a far poorer grade. Each stage depends on subtle differences in the surface chemistry of the constituent minerals present in the ore as discrete grains.

The flotation process is unquestionably of great economic importance, but it has never caught the popular imagination and, indeed, is largely unknown to many scientists. One reason is that big flotation plants, like that shown in figure 2, are located chiefly in the somewhat remote areas where metalliferous ores are mined. Another is that the process did not come about as a sequel to fundamental research, but was developed over the years by unspectacular empirical methods. As a result, basic work in this field has long been occupied with the problem of explaining, first of all, why the existing process works so well.

It seems possible that the stage has now been reached when any substantial further elaborations of the flotation process will demand a more profound understanding of its fundamentals. Up to the present time, however, a common result of research into existing examples of the process has been to expose unsuspected complexities. An example of what might be called 'science in pursuit of technology' is provided by the classic flotation system—the extraction of galena (PbS) using xanthate as the collector. Despite a long history of laboratory study, this system is still yielding surprises and fresh problems under the scrutiny of modern research techniques. The present state of the theory is discussed later in this article.

M. G. Fleming, *Ph.D.*
Was born in Canada in 1913 and educated at Queen's University, Kingston. At the beginning of the War, he was chief metallurgist of a Canadian gold mine. After service in the R.C.A.F., he joined the staff of Imperial College, London, in 1946 and served as Lecturer, Senior Lecturer, and Reader in Mineral Dressing. In 1961, he was appointed as the first Professor of Mineral Technology. His personal research has been mainly in the field of flotation.

J. A. Kitchener, *D.Sc.*
Was born in 1916 and educated at Bec School, London, and University College, London. His first research was on photochemistry, but as Lecturer and, later, Reader in Physical Chemistry at Imperial College, he has worked on a wide range of problems, including ion-exchange phenomena and colloid stability. He is now Reader in the Science of Mineral Processing in the College.

Empirical development of a modern technology

Although several rudimentary flotation processes were tried during the latter half of the nineteenth century, they lacked the two most essential features of the modern process—the use of minimal quantities of collectors, and the injection of a stream of air bubbles to provide an extensive interface to carry off the grains rendered hydrophobic by the collector. These ideas first appeared in a famous British patent granted to H. L. Sulman, H. F. Picard, and J. Ballot in 1905. They were quickly exploited for treating the vast and complex deposits of zinc and lead sulphides in the Broken Hill district of Australia, and within a remarkably short time froth flotation was brought to a high pitch of metallurgical efficiency.

In the early days, impure fatty acids or eucalyptus oil were used as collectors for the simple reason that they were found to work. Galena could be floated off first from an alkaline slurry of the crushed ore; then acid and copper sulphate were added to activate sphalerite (ZnS). Oxidized minerals, such as anglesite ($PbSO_4$), could be activated by sodium sulphide. The metallic minerals were thus, in turn, rendered hydrophobic, and therefore floatable, before the gangue of siliceous minerals. Nevertheless, under other conditions, quartz, silicates, fluorides, and oxides of metals can be floated with equal success by use of fatty acids, traces of metallic salts being needed to activate the minerals if they do not themselves provide suitable cations.

The reasons for the preferential deposition of fatty acid collectors on sulphides are still not fully elucidated and were certainly quite unknown when the process was introduced. The pioneer mineral technologists who developed the successful large-scale process were inventors rather than scientists; they achieved their results on the basis of an elementary knowledge of chemistry and physics with the aid of trial-and-error tests.

The next major invention was the introduction of xanthates as collectors for sulphide minerals. Structurally, xanthic acid can be regarded as a sulphur derivative of carbonic acid $\left(\begin{matrix} & O & \\ & \| & \\ HO- & C & -HO \end{matrix}\right)$. Potassium ethyl, isopropyl, butyl, and amyl xanthates $\left(\begin{matrix} & & S & \\ + & - & \| & \\ K & S- & C & -O-R \end{matrix}\right)$

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

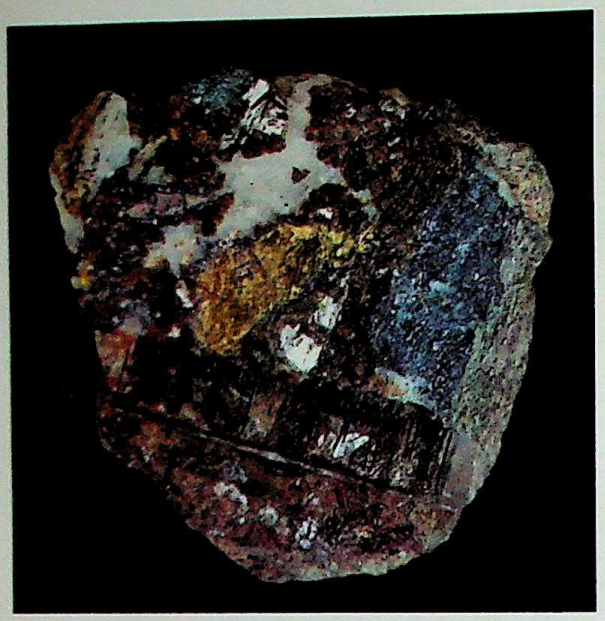


Figure 1 An ore containing galena (grey), sphalerite (brown), pyrite (gold), and quartz (white).

(R is the alkyl group) are the salts most commonly used as collectors and, like many thiols, they form practically insoluble precipitates with salts of heavy metals. There appears to be no record of how this class of compound was hit upon. C. L. Perkins in 1919 had the idea of using as collectors, in place of complex oils, sparingly soluble organic compounds that would be relatively easily oxidizable. Diphenyl thiourea was one of several substances specifically cited. This concept nowadays seems somewhat relevant to the action of xanthates, but no explanation was offered for it in the patent. Xanthates were specifically patented as flotation collectors by C. H. Keller in 1923, but again without any theoretical justification for the choice. They are not chemicals that are commonly found in the laboratory, but were mentioned in contemporary literature as accelerators for vulcanization of rubber as well as for the production of artificial silk by the viscose process. It seems likely that their collector properties were discovered by blind trial.

Despite the empirical manner of their introduction, the use of xanthates was an important advance because they provided a new order of selectivity, being discriminating collectors for heavy-metal sulphides. Following the introduction of xanthates, other related compounds, such as dithiophosphates, were found to have collector action. However, no new principle was discovered, and the mineral technologist's dream of a series of specific collectors for different minerals has never materialized. For economic reasons, xanthates still hold their own.

Early researches

The success of xanthates and other synthetic collectors stimulated basic research into the mechanism of flotation. In 1928, A. F. Taggart developed a bubble-contact apparatus for determining the angle of contact at the three-phase boundary between gas, solution, and the polished surface of a mineral specimen. However, the results were unreliable because the difficulty of avoiding contamination of the surfaces by adventitious grease from the air, water, or hands was not appreciated. A satisfactory technique, almost comparable with aseptic surgery, was introduced by I. W. Wark in Melbourne, who from 1930 to 1939 led a team of physical chemists in applying accurate techniques for the first time to the scientific study of flotation.

During this period an intense competition developed between research workers in Australia and in America, and basic discoveries followed one another in rapid succession. A. M. Gaudin had demonstrated the importance of pH in 1929, and soon, by a brilliant piece of deduction, Taggart recognized that all the soluble collectors have polar and non-polar groups within the same molecule. I. W. Wark, A. B. Cox, and K. L. Sutherland showed that flotation recovery is directly related to the magnitude of the contact angle and that the maximum angle obtainable when a mineral is saturated with a given collector is independent of both the underlying mineral and of the polar group linking the collector to it. It depends only upon the nature of the hydrocarbon chain of the collector.

Thus there emerged the now familiar picture of xanthate ions anchored by their polar groups to a metal cation on the surface of the mineral, so presenting a hydrophobic palisade of alkyl groups to the solution. That much seemed clear enough; but the mechanism of attachment of the xanthate to the sulphide mineral—which is obviously the key to the selectivity of the collector—remained obscure, and an amazing polemic developed around this point.

Figure 2 The flotation section in the Butte, Montana, concentrator. (By kind permission of the Anaconda Company.)

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

The Australian school attributed attachment to adsorption. As the xanthate cannot be washed off with water, but can be displaced by soluble sulphides, the most plausible hypothesis pictures xanthate anions taking the place of sulphide ions in the exposed faces of the PbS lattice (figure 3). Taggart's American school, on the other hand, insisted that the collector coating is formed by a stoichiometric double decomposition reaction governed by classical mass-action principles, and based on the low solubility of heavy-metal xanthates. Heavy-metal xanthates are very sparingly soluble compounds, but when an approximate value for the solubility product of lead ethyl xanthate was determined, it became apparent that PbS in bulk could not react with any practicable concentration of xanthate. Nevertheless, such was the heat of the controversy that some surprising distortions of the law of mass action were invoked, such as the suggestion that the ionic product for material on the surface of PbS should be evaluated by taking the local ionic concentrations within the crystal lattice.

An alternative hypothesis was that oxidation of galena to more soluble lead salts might be necessary before it could react with xanthate; for example

$$PbS + 2O_2 \rightarrow PbSO_4$$

followed by

$$PbSO_4 + 2KEtX \rightarrow Pb(EtX)_2 + K_2SO_4, \text{ where } X = \text{xanthate.}$$

In support of this theory, A. F. Taggart, T. C. Taylor, and A. F. Knoll showed that traces of sparingly soluble lead salts could be leached from galena in the presence of air, and that when the same galena is treated with xanthate, substantial quantities of anions are given out to the solution, including sulphate, thiosulphate, hydroxide, and carbonate. Furthermore, these anions together are roughly equivalent in amount to the xanthate taken up.

Wark countered this telling point by claiming that galena can be floated with nitrogen in the absence of oxygen and that collector attachment can take place under conditions that do not permit the solubility product for lead xanthate to be exceeded. There was also the claim that the collector coating cannot be removed by organic solvents that readily dissolve ordinary lead xanthate. Suspicion was thrown on the analytical methods then available for measuring the small quantities of compounds exchanged between the solid and the solution, while, on the other side, the difficulty of adequately excluding oxygen from bubble tests raised doubts about Wark's claim. In the end, the world events of 1939–45 overshadowed this polemic, and it quietly died of neglect.

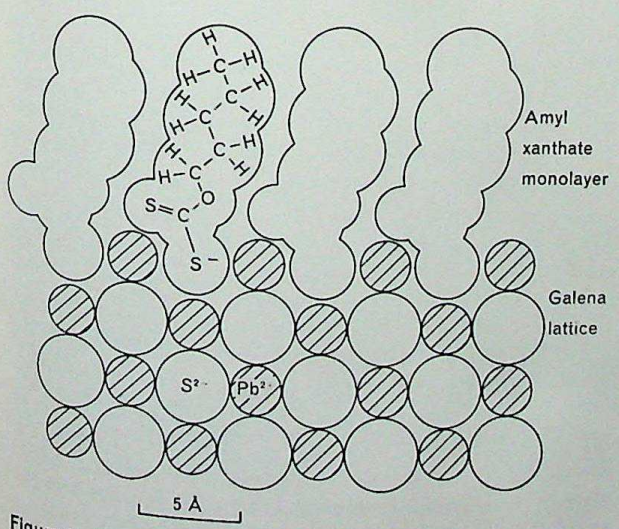


Figure 3 Conventional diagram of a complete xanthate monolayer sorbed by anion exchange on a galena surface.

Post-war investigations

When flotation research was resumed after 1945, a variety of powerful new techniques was available for a fresh attack on the problem.

Gaudin and his co-workers at the Massachusetts Institute of Technology combined measurements of the surface area of powdered minerals with determinations of the amount of collector taken up; these could now be reliably determined by using radio-tracers. The results obtained with various minerals and different collectors proved conclusively that, with the minimal dosages of collector employed in practical flotation, the amount taken up is commonly a small fraction of what would be required to form a close-packed monomolecular layer over the mineral grains.

This result demanded some modification of the conventional model. However, the text-book monolayer was admittedly associated with the saturation condition at rather high concentrations of collector. It thus seemed reasonable to assume that a sparse, fractional, but presumably uniform monolayer would yield a smaller but still finite contact angle sufficient for practical flotation. This concept was shaken in 1957 when I. N. Plaksin and his co-workers first published in English the results of work that had been in progress in Russia for some years [1]. Using micro-autoradiography with xanthate labelled with the weak β-emitter ^{35}S, the Russians gave visual evidence that the sorption of xanthate occurs not uniformly but highly irregularly on the galena. The coating is dense on some faces and on some grains, and sparse or non-existent on others. It frequently presents a spotty appearance where multilayers have built up locally on an otherwise uncoated surface.

Subsequent work has indicated that irregular deposition of collectors may be the general rule. Plaksin has reported it also with sphalerite + xanthate, fluorite + sodium tridecylate, and in the deposition of activating Fe^{3+} on cassiterite (SnO_2), and Th^{4+} on calcite ($CaCO_3$). In the present writers' laboratory very similar autoradiographs have been obtained with galena treated with $Na_2{}^{35}S$, and calcite + potassium oleate (^{14}C). Most recently, calcite crystals immersed in $Na_2{}^{14}CO_3$ have yielded patchy autoradiographs by the pure self-exchange of anions (figure 4).

It now seems most likely that the non-uniform response of mineral grains to these various reagents is a direct consequence of their heterogeneity in chemical composition or physical condition. As the grains are obtained by crushing impure, imperfect, crystals, it is to be expected that certain parts, such as shattered zones or impurity regions, should be more reactive than others for both energetic and kinetic reasons. Galena, in particular, consists of highly strained and distorted crystallites that belie its beautiful cleavage (figure 5).

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

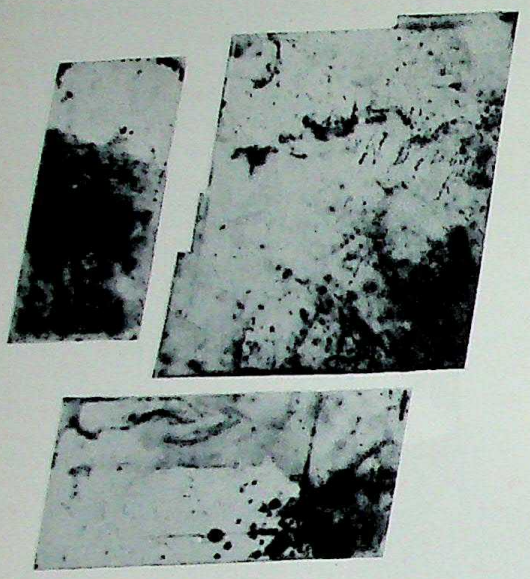


Figure 4 Autoradiographs of three cleaved crystals of Iceland spar (calcite, $CaCO_3$) after treatment with a dilute solution of sodium carbonate labelled with ^{14}C. Dark areas show where carbonate has exchanged. (×6)

At about the same time as they published their radiotracer work, Plaksin and his colleagues finally settled the long-standing controversy as to whether or not oxygen is a necessary participant in the attachment of xanthates to sulphide minerals [2]. The experimental difficulties were overcome by working on a larger scale with an elaborate apparatus in which mineral could be ground, sized, conditioned with reagents, and then floated in a controlled atmosphere. The Russians proved that there is a close correlation between the oxygen available, the amount of collector taken up, and the final floatability of the mineral.

The amount of oxygen required for flotation has apparently not been compared with the surface area involved, but rigorous high-vacuum techniques are not required to avoid floatability [3], which suggests that more than a chemisorbed monolayer is involved. In fact, it is known that the interaction of galena with oxygen, even at room temperature, is not confined to the outer layer, but is progressive, though slow. Some admirable chemical work by B. Reuter and R. Stein [4] on PbS powder has shown that the predominant reaction at room temperature in the presence of water is formation of a basic thiosulphate

$$PbS + \tfrac{1}{2}O_2 \rightarrow PbO + S$$

$$PbO + H_2O \rightarrow Pb(OH)_2$$

$$PbO + 2S + O_2 \rightarrow PbS_2O_3$$

By an entirely independent method—infra-red spectroscopy—R. G. Greenler [5] and J. Leja, L. H. Little, and G. W. Poling [6] also identified lead thiosulphate on slightly oxidized galena. Long ageing in air leads to lead sulphate and basic carbonate as well. All these oxidation products are far more soluble than lead sulphide and can undergo double decomposition reactions with xanthates at normal flotation concentrations, yielding lead xanthate.

Further confirmation of this scheme for the chemistry of the system has been obtained in the writers' laboratory by O. Mellgren [7], who has found by direct calorimetry that the heat of sorption of xanthate by crushed, washed galena corresponds to the reaction with lead thiosulphate. He has also proved that the oxidation layer on galena readily undergoes anion exchange with sulphate or carbonate, releasing thiosulphate.

There can be no doubt, therefore, that double decomposition reactions with oxidation products do take place, and they are presumably the cause of the local dense patches seen in the autoradiographs. But there is still a mystery about the nature of the ultimate hydrophobic film, for there remains one awkward fact. This is that, although most of the reaction products can be extracted from floated galena with organic solvents, the mineral retains a hydrophobic surface. Radio-tracer tests also show some activity that cannot be removed by solvents.

Electrochemical factors

When I. N. Plaksin and R. Sh. Shafeev [8] considered the role of oxygen in this system, they drew attention to another significant feature. Galena, as its metallic sheen indicates, is an electrical semiconductor. Therefore, as it is also non-uniform in properties because of non-stoichiometry, impurities, and strains, it presents areas of different electrochemical potential. This has been demonstrated with a micro-probe electrode by B. Kamienski and co-workers in Poland [9]. Consequently, when in contact with electrolyte solutions, it shows phenomena similar to local-cell corrosion of metals, some areas being relatively cathodic and others anodic. Plaksin and Shafeev suggested that anionic reagents such as xanthate would preferentially attack the most positive areas. According to these authors, the function of oxygen in the system is to mop up free electrons from the conduction bands (galena in the natural state being an *n*-type semiconductor) and thereby to raise the potential of anodic areas to the point where xanthate is chemisorbed. Reuter and Stein [4] have, indeed,

Figure 5 Interference micrograph of a typical cleavage face of natural galena, showing disturbed structure. The lines can be regarded as vertical contours at $\frac{1}{4}$ μ intervals. (×35) (By courtesy of Professor S. Tolansky.)

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

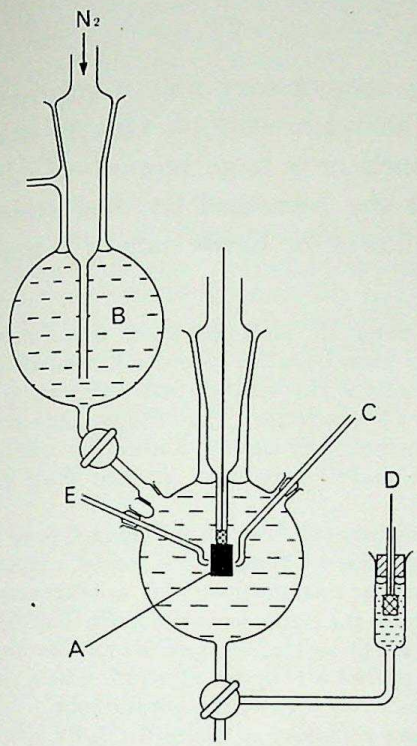


Figure 6 Diagram of cell used for studying the effect of electrode potential on bubble contact [10]. A, galena electrode; B, solution preparation; C, D, auxiliary electrodes; E, bubble contact tube.

proved by measurements of the electronic properties of PbS films that it passes from *n*-type to *p*-type when exposed to oxygen. Plaksin and Shafeev consider that the *p*-type lattice could assimilate the electron from a xanthate ion. They also mention the possibility that, with more oxygen, the xanthate might be 'further oxidized' to dixanthogen $(EtX)_2$. Actually, this step would merely involve combination of two adjacent chemisorbed EtX· radicals.

It was realized by R. Tolun that these hypothetical electronic processes in galena should be reflected in its electrochemical potential. Using crystals of galena as electrodes in cells from which air could be excluded (figure 6), R. Tolun and J. A. Kitchener [10] proved that addition of oxygen shifts the electrochemical potential to more positive values until it reaches the value at which xanthate ions from solution are oxidized to dixanthogen. In other words, galena acts as an electron-transfer catalyst for the reaction

$$2EtX^- + \tfrac{1}{2}O_2 + H_2O \rightarrow (EtX)_2 + 2OH^-$$

If only a small dose of oxygen is admitted, the potential slowly drifts back because of the reducing action of the underlying galena. The redox reaction

$$2EtX^- = (EtX)_2 + 2e$$

is reversible on the surface of a metallic conductor. The oxidation product, dixanthogen, when prepared in bulk, is a sparingly soluble oil which adheres to and spreads over galena, as A. A. Golikov [11] has demonstrated. In the experiments of Tolun and Kitchener it was found that the galena would not form contact with a captive bubble until the potential corresponding to a saturated solution of dixanthogen was reached. If the potential was again made slightly more negative (reducing), by deliberate polarization or long standing with exclusion of oxygen, bubble contact was lost; it could be restored by admitting more oxygen. In other experiments it was proved that a film of lead xanthate alone does not give a surface that will produce flotation, even though lead ethyl xanthate is a sufficiently non-polar compound to be appreciably soluble in ether. Furthermore, if it is formed on a non-catalytic substrate such as lead sulphate instead of galena, it does not become hydrophobic even in the presence of air.

It seems, therefore, that most of the evidence fits the hypothesis that the practical flotation surface is a mixed layer of lead xanthate and dixanthogen. This conclusion is entirely consistent, for example, with the infra-red spectroscopic evidence. The proportions of xanthate to dixanthogen are not yet known, but it would not be surprising if they turned out to be roughly 1 : 1 in the most stable film, for physical monolayer complexes of ionic surfactants with non-polar oils are well known in surface chemistry.

Conclusion

If flotation were a new invention, our present understanding of the surface chemistry of galena would scarcely be considered an adequate basis for a vast industry with plants treating up to 50 000 tons of lean and complex ore per day. The past success of this empirically based process must be almost unique in modern technology; but, clearly, its ultimate potentialities will not be known until the surface chemistry of a wide range of mineral species has been more fully explored.

References

[1] Plaksin, I. N. *Int. Min. Processing Congr.* (*Lond.*), 253, 1960.
[2] Plaksin, I. N. and Bessonov, S.V. *Proc. 2nd Int. Congr. Surface Activity, Lond.*, 3, 361, 1957.
[3] Beebe, R. R. and Westley, C. E. *Trans. Amer. Inst. min.* (*metall.*) *Engrs*, 220, 9, 1961.
[4] Reuter, B. and Stein, R. *Z. Elektrochem.*, 61, 440, 450, 1957.
[5] Greenler, R. G. *J. phys. Chem.*, 66, 879, 1962.
[6] Leja, J., Little, L. H., and Poling, G. W. *Trans. Instn Min. Metall., Lond.*, 72, 407, 1963.
[7] Mellgren, O. *Ibid.*, 72, 674, 1963; and private communication.
[8] Plaksin, I. N. and Shafeev, R. Sh. *Ibid.*, 72, 715, 1963.
[9] Szeglowski, Z. *Proc. 3rd Int. Congr. Surface Activity, Cologne*, 2, 110, 1960.
[10] Tolun, R. and Kitchener, J. A. *Trans. Instn Min. Metall., Lond.*, 73, 313, 1964.
[11] Golikov, A. A. *Sov. J. Non-Ferrous Metals*, 2, 19, 1961.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

The development of the travelling wave tube

R. Kompfner

Most of the devices that are used for amplifying radio waves operate over only a relatively narrow waveband. The travelling wave tube is untuned, and can therefore work over a very wide waveband. This makes it ideal for amplifying television channels or a large number of telephone channels. This article describes the modern versions of the tube and its uses, which include communication with rockets and by way of artificial satellites of the Earth, such as Telstar.

Introduction

The travelling wave tube is the heart of most microwave communication systems. The rôle which it plays is of such critical importance that it is the rapid improvement in the performance of travelling wave tubes in recent years which has largely determined the overall capability of microwave systems. The story of the invention of the travelling wave tube during World War II has already been told [1]. It was obvious from the start that the travelling wave tube (figure 1) would not play any part in that war. It seemed merely an interesting variation on the theme of amplifying microwaves by means of the interaction between such microwaves and an electron beam. Its potential was seen only dimly, if at all. Its range of capability and variety of functions are the result of a series of developments, that is to say, ideas carried through to reality, ideas that happened 'in parallel' as well as 'in series', and that needed about ten years to emerge. Its performance can now be predicted with a degree of accuracy that is rarely encountered in devices of comparable complexity.

The travelling wave tube's outstanding property is that it is able to amplify very wide bands of frequencies. In this it differs from most other amplifiers, which generally include a resonant element in their construction. Such an element increases the sensitivity, but since the resonance implies a preferential response to a particular frequency, the range of frequencies which it can amplify is limited.

The frequency interval (the bandwidth) used in a transmission system is a direct measure of the amount of information which can be accommodated. Thus a telephone channel requires a bandwidth of 4000 c/s, a television picture about 3 000 000 c/s. For example, one can transmit three television channels and 2000 telephone channels in a bandwidth of 20 Mc/s.

The broad-band characteristic of the travelling wave tube stems from the fact that there is no resonant element in its make-up. As shown in figure 1(a), the signal which is to be amplified propagates along a helix of wire, and an electron beam passes along the axis of the helix. The velocity of the electron beam is arranged to be approximately equal to the velocity of propagation of the signal wave along the helix. Since electrons must move at a velocity less than that of light (in a typical medium-power travelling wave tube the velocity might be one-tenth that of light), whereas electromagnetic waves travel with a phase velocity equal to that of light when in free space, or faster in most common waveguides, special provisions must be made in order to slow down the wave. The helix is the simplest and the most frequently used 'slow wave circuit'. The effective reduction in velocity is obtained very simply, namely by making the signal wave travel a greater distance than the electron beam.

The signal is transferred from some standard form of waveguide to the helix by means of a special coupler, shown as a rectangular tube in figure 1(b); another coupler is used to transfer the signal from the helix. The electron beam is formed by an electron gun, and at the other end of the tube reaches a collector electrode whose sole function is to remove the electrons from the tube.

The signal wave propagating along the helix affects the motion of the electrons in the beam—it bunches them—and the bunches in turn deliver energy to the wave so as to make it grow. This growth can be large, and in fact it varies approximately exponentially with distance. To a first approximation, it is independent of the frequency of the wave. So it comes about that the travelling wave tube is a wide-band amplifier with a power gain of ten thousand or more, over frequency bands of more than an octave, which may in practice mean thousands of megacycles.

These characteristics have led to the adoption of the travelling wave tube in a wide variety of systems, ranging from microwave telephone, television, and other

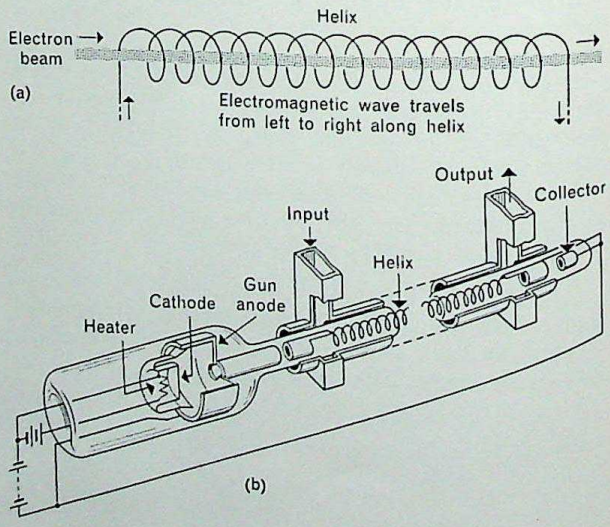


Figure 1 (a) Principle of the travelling wave amplifier. (b) Portion of the travelling wave amplifier pertaining to electronic interaction with radio-frequency fields and radio-frequency gain. The length of the tube will be approximately 25 cm for a tube operating at 6 kMc/s.

R. Kompfner, Dipl. Ing., D.Phil.

Was born in Vienna in 1909, and received a degree in Architecture from the *Technische Hochschule* there. During the war worked for the Admiralty, first at Birmingham University and then at the Clarendon Laboratory, Oxford. Since 1951 he has been a member of technical staff at Bell Telephone Laboratories in the United States.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

data transmission links to satellite communication systems; and from radio-astronomy to missile guidance. Some of these applications will be discussed in later sections. Before doing so, we shall consider the mode of operation and the performance of travelling wave tubes in more detail.

Basic properties of the travelling wave tube

A travelling wave tube can be described by a number of parameters of major and minor importance. These are the gain—the ratio of signal output power to signal input power; the bandwidth—the frequency band over which the gain does not deviate from its maximum by more than, say, one-half; and the maximum power output and efficiency, the latter defined as the ratio of the maximum power output to the d.c. input. All these quantities are functions of the geometry of the device, of the frequency, of the electron beam current and beam voltage, the magnetic field used to focus and hold together the beam, and of other less simply described parameters.

The slow-wave circuit

The 'circuit' is the part of the tube that carries the signal to be amplified. Its original form was a helix of metal wire, and the helix is still the most widely used circuit, although for extremely high power, or exceptionally short wavelengths, other types are used.

The function of the circuit is to propagate an electromagnetic wave at such a velocity that it can interact strongly with an electron beam which has been accelerated, typically, to a few thousand volts. In order to achieve such strong interaction, the circuit field must have a consistent effect on any individual electron. This implies that the phase velocity v of the wave on the helix must be very close to the electron velocity, as otherwise the electron would experience a rapidly alternating force which could not have any appreciable net resultant. In terms of the electron beam potential V_0 this condition is achieved when

$$v = (2e/m)^{\frac{1}{2}} V_0^{\frac{1}{2}} \qquad \ldots\ldots(1)$$

where e/m is the charge-to-mass ratio of the electron. It is a fact—and a fortunate one—that the axial phase velocity of a helix is independent of frequency over a very wide range. Its propagation characteristics can be described pretty well by assuming that the wave travels round the wire with the velocity of light.

The rate of progress of the wave along the length of the helix in the axial direction will of course be slowed in proportion to the ratio of the pitch of the helix to its circumference.

The interaction between the wave on a helix and a beam can be expressed in terms of a coupling impedance K. This relates the axial field E_z to the signal power P flowing along the helix:

$$K = \frac{1}{8\pi^2} \frac{E_z^2}{P} \left(\frac{v}{f}\right)^2$$

where f is the frequency.

In general it is desirable to get the largest possible value of K, as this improves the gain attainable and also the efficiency of the tube. It turns out that if the helix radius a is small, the impedance K is approximately equal to $30n$ ohms, where n is the number of turns per wavelength. If the radius a is large, the field is small (figure 2) and the effective value of K varies with the radius, and may be very low on the axis. An excessively large helix radius is therefore to be avoided; on the other hand, if a is too small, it is not possible to send a very large current beam through the helix. Thus one finds that there are optimum proportions for a helix. Most tubes are built so that the quantity $2\pi af/v$ is between 1 and 2, a compromise which yields the highest effective coupling for the largest electron beam.

Coupling and loss

Many types of coupling between the helix of a travelling wave tube and the external input and output circuits have been devised. Naturally, they depend on whether the external circuit uses waveguides or coaxial transmission lines, and we need not go into these details. What is important for our purposes is that, because of the enormous bandwidth over which a travelling wave tube can amplify, and its large gain, even small reflections at the output and input would cause the tube to oscillate at numerous frequencies unless precautions were taken. What is done is to introduce a distributed loss along the helix, somewhere in the first quarter to one-third of its length, sufficient to attenuate a signal in the absence of the electron beam to about one-millionth. This, surprisingly, has little effect on the gain in the forward direction of the tube, but it attenuates a backward-travelling reflected wave so much that oscillation becomes impossible at any frequency, unless feedback external to the tube is introduced deliberately.

The explanation for this remarkable behaviour is that in the forward direction, the signal is transported not only by the circuit, but also by the beam. When the circuit passage is blocked, the signal can still be transmitted, with little loss, by the beam. However, in the reverse direction the beam plays no part whatsoever, because it is completely out of synchronism with the backward wave. The backward wave is therefore almost completely absorbed by the attenuator. The realization of the benefits of this attenuation and its quantitative evaluation was one of the triumphs of the analysis due to J. R. Pierce [4] and constitutes perhaps the most important single step towards making the travelling wave tube a practical device.

The electron beam

One of the major problems in the design of a travelling wave tube lies in the control of the electron beam. The diameter of the helix is generally less than one-twentieth of the free-space wavelength corresponding to the

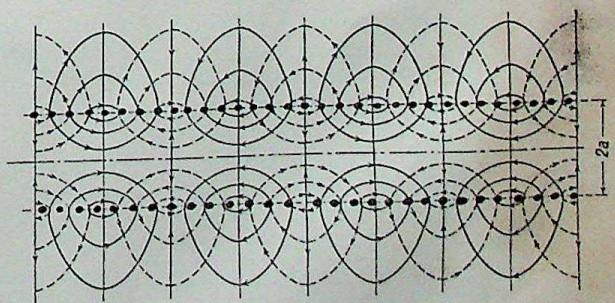


Figure 2 A sketch of the fields on a helix with a large radius. The solid lines are electric field and the dashed lines are magnetic field.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

average frequency for which the tube is designed. Thus a travelling wave tube designed to operate in a band centred on 6000 Mc/s, where the free space wavelength is 5 cm, would use a helix with a diameter of only 2·5 mm. On the other hand, it might well be 25 cm long. Now the electric field produced by the helix, which modulates the electron beam current, is strongest close to the helix. It is therefore generally desirable to use a beam diameter which may be only 15 per cent smaller than the internal diameter of the helix. It is of great importance that the electron beam should not suffer any appreciable interception by the helix, which is a relatively frail structure and can readily overheat and even melt. In the example considered, the location of the electron beam must therefore be controlled with an accuracy of around 0·1 mm over a length of 25 cm. Sophisticated techniques are thus required both in launching the electron beam, and in guiding it once it has entered the helix.

The beam nowadays produced in a 'Pierce' electron gun is focused and held together either by a uniform or an alternating magnetic field [5]. The Pierce gun is a structure which was known and used before the advent of the travelling wave tube. It yields the maximum possible electron current from a given cathode in the form of a collimated beam. In the absence of a magnetic field, this beam would subsequently diverge and spread because of the charge of the electrons. To counteract this tendency, the earliest tubes were completely immersed in a uniform magnetic field of a few hundred oersted produced by coils or solenoids through which an appropriate direct current flowed. It was found experimentally that more and more electron-beam current could be transmitted through the helix to the collector, and more gain and power obtained from the tube as the magnetic field near the gun was reduced. Eventually, C. C. Wang realized that the optimum was achieved when the gun itself was in an almost field-free region, with the magnetic field rising almost abruptly to a maximum and constant value near the point where the beam emerging from the Pierce gun had its minimum diameter [6] (figure 3). Under these conditions it turns out that one obtains an almost perfect balance of the three forces acting on every electron in the beam. These are the electrostatic repulsion due to the presence of all the other electrons in the beam, acting radially outwards; the Lorentz force due to the magnetic field; and centrifugal force due to the circling motion of the electrons, acting outwards. Furthermore, it can be shown that, for a given magnetic field, a minimum beam diameter is obtained. Last, but not least, it can be shown that under these conditions all electrons move with equal axial velocities.

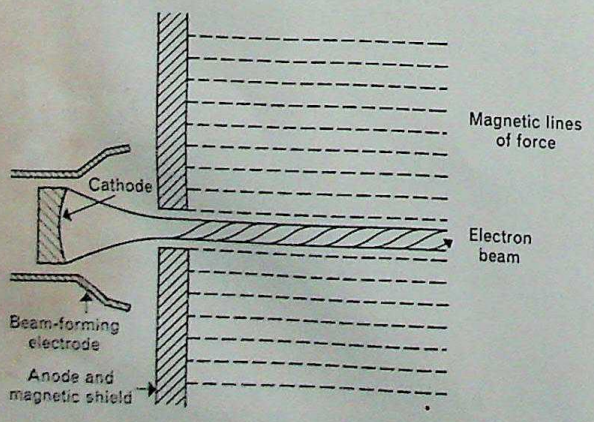


Figure 3 Brillouin-flow type of electron gun ('Wang gun').

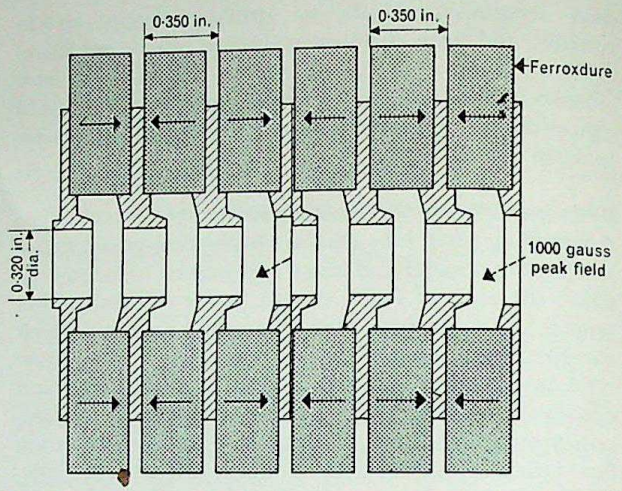


Figure 4 Assembly of Ferroxdure magnets and Permalloy pole-pieces used for focusing a TWT electron beam.

We have already seen that it is vital that the electrons should be in synchronism with the wave on the circuit. The fact that in this situation all electrons progress along the length of the helix with the same velocity is therefore an important feature of this type of focusing for the achievement of efficient interaction between the whole electron beam and a travelling wave.

The method of producing an electron beam just described is known as 'Brillouin flow', after L. Brillouin, who first analysed electron flow in combined electric and magnetic fields [7].

Periodic focusing

In many cases there are two problems concerned with the current required to flow in the solenoid in order to produce the magnetic focusing field. These problems are providing the current, and keeping it stable. For this purpose, permanent magnets are frequently used. In order to provide the long and uniform field required by a typical travelling wave tube, large and heavy magnets are necessary, which are very expensive and also possess large stray fields that interfere with the focusing of adjacent travelling wave tubes and with other electronic equipment. The introduction of periodic focusing using many small permanent magnets to produce an alternating magnetic axial field has therefore been of considerable practical importance [8, 9] (see figure 4). It can be shown that such a field will focus a beam almost as well as a uniform field equal to the root-mean-square alternating field. The weight and the stray fields of an assembly of magnets necessary to produce the required alternating field are a small fraction of those of a uniform-field magnet or of a solenoid and its power supply.

The collector

A necessary, but relatively simple, component of every travelling wave tube is the collector, which collects the

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

electron beam after it has traversed the helix and given energy to the wave. One might, naively, think of holding the collector near cathode potential, collecting the electrons with velocities near zero, and thus achieving very high overall efficiency of energy conversion. In the absence of any signal on the helix it is indeed possible to collect nearly all the beam with almost zero velocity. In the presence of a signal, however, a fraction of the electrons are speeded up and a greater fraction is slowed down; in order to collect all of them, the collector has to be kept at a potential that is about one-third to one-half of the beam potential. Nevertheless, doing this increases the overall efficiency considerably, which is of some importance in travelling wave tubes used in communication satellites.

Functions and performance

The growing wave

The growth of a signal injected at the input end of a uniform helix is approximately exponential. (Its exact form is known but will not be given here.) Let us define a parameter C, called Pierce's coupling parameter [4]:

$$C^3=(KI_0)/(4V_0)$$

The power gain G of a uniform helix travelling wave tube can best be described in decibel notation. If P_{in} is the input power to an amplifier and P_{out} is the output power, the gain $G=10\log_{10}(P_{out}/P_{in})$ decibels or $G=-9{\cdot}54+47{\cdot}3CN$ decibels, where N is the number of wave lengths.

As we have noted, in practice there will always be some attenuation along the helix, very heavy for a short portion of it, in order to suppress a tendency to oscillation. Also space-charge forces and some lack of uniformity in the electron velocities have to be taken into account. This can be done with accuracy and confidence, and experiment and theory agree exceedingly well.

Power and efficiency

What is the highest power one may obtain from a travelling wave tube? As the energy of the wave grows and begins to approach that of the electron beam, a considerable fraction of the beam must have been slowed down, since that is where the energy came from. As a result, wave and beam can no longer be said to travel at the same velocity, and the process of energy transfer ceases; indeed, it reverses, and from a certain signal level on, the power in the wave decreases again. The power level at this point is, obviously, the largest power obtainable from a travelling wave tube, and a simple theory shows that it approximately equals I_0V_0C. Hence the efficiency is approximately C.

In practice, space-charge forces play an important part, as also does the velocity distribution of the electrons; efficiencies of 40 per cent have, however, been measured, as well as microwave power levels of many thousands of watts.

Noise

An ideal amplifier would introduce no noise, but merely amplify the signal faithfully. Any real amplifier, however, introduces extra noise in the process of amplifying a signal, and it has become customary to describe an amplifier in terms of its noise figure F, where

$$F=\frac{\text{ratio of signal to noise at input}}{\text{ratio of signal to noise at output}}$$

The main sources of noise in a travelling wave tube arise from the discreteness of the electron charge (the 'shot noise') and from the fact that the electrons come from a hot cathode (at temperature T_c) with a Maxwellian distribution of velocities. Much is now known of how these sources of noise come to generate fluctuations in the electron beam current and beam velocity, and how they are transferred to the circuit—the helix—where they appear as noise competing with the signal.

Early theories of the noise behaviour were not very successful. It was not until it was realized that an electron beam can support and transmit space-charge plasma waves, just as a transmission line or a waveguide transmits electromagnetic waves, and that the noise enters into the tube by way of two essentially uncorrelated noise signals (namely shot-noise current and thermal velocity excitation) that theory and practice began to converge.

A straightforward (small-signal) theory, taking into account the propagation of the above-mentioned electron plasma waves in the electron beam, gives the following expression for the minimum achievable noise factor:

$$F_{min}=1+(4-\pi)T_c/T$$

Oxide cathodes, as generally used in travelling wave tubes, are usually heated to somewhere near 1000°K, and one finds that the best electron-beam amplifier, whether a travelling wave tube or any other kind, should have a noise figure about four times worse than ideal.

In actual fact this has been achieved, and even surpassed. A result which is better than the best theoretically possible indicates that the theory is still at fault. A more complete theory, no longer based on small signals, especially near the crucial region very close to the cathode, is able to account for the observed noise figures, but it is very complicated and difficult to apply generally.

None the less, the gradual improvement of the noise figure from somewhere near 1000 in 1946 to 2 or 3 at the present time shows well how advances in understanding went hand in hand with increasing sophistication in design and greater accuracy of construction to produce one of the more sensitive, wide-band, and high-gain amplifiers now known.

Uses of travelling wave tubes

In microwave relays

The travelling wave tube has a broad bandwidth, high gain, and a low noise factor, and these make it well suited for microwave relays for television and for many-voice channels. This was indeed its first use on a large scale [2]. Today, there are microwave networks using travelling wave tubes in many countries, including England, France, Germany, Japan, and the United States. The long-distance traffic in, for example, the United States is carried by means of cables and microwave radio; the latter originally used microwave triodes but is now turning to travelling wave tubes. One system, the TH system, is operated in the 5925–6425 Mc/s band, and is arranged to provide eight two-way channels, each capable of transmitting 1800 telephone messages, or one television channel and 420 telephone messages.

It may be of some interest to examine the characteristics

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

of the particular tube (type 444a) designed for this system. These are:

Helix voltage	2400 volts
Collector voltage	1200 volts
Beam current	40 milliamperes
Magnetic field (uniform) ..	600 gauss
Output power	5 watts
Gain at 5 watt level ..	30 db
Noise figure	28·5 db

This tube can put out as much as 11 watts, but as this causes distortion in the repeaters, the power level is held at 5 watts.

The construction of the tube is conventional. The tungsten helix is supported by three ceramic rods, to which it is bonded by means of a glaze. The gun is a convergent Pierce gun providing $0{\cdot}3 \times 10^{-6}$ A/V$^{\frac{3}{2}}$ from a current density of 200 mA/cm^2 at the cathode. The uniform magnetic field of 600 oersted is provided by two bar magnets of Alnico; it is higher than the Brillouin field because there is a flux of about 20 oersted at the cathode in order to reduce noise.

Many years of development have gone into the making of this tube. Every feature of the tube, such as the helix itself, its support, the location and magnitude of the loss, the electron gun, and the magnetic focusing field distribution, was studied with a wide range of parameter variations, with life tests, and under a wide variety of conditions, until finally a design was evolved which would give optimum performance under all conditions that the tube was ever likely to meet [10, 11].

In satellite communications

Satellite-communications repeaters differ from microwave repeaters on Earth only in the following respects. The cost of launching a single repeater is so high, and so dependent on the total weight to be placed in orbit, that it becomes very important to ensure very long life, which implies high reliability, and also to obtain maximum performance with minimum weight. Most of the weight of a satellite is in its power supplies—solar cells, storage batteries, and conversion units. Thus one needs a source of microwave power which is efficient, long-lived, and reliable, gives high gain and adequate bandwidth, and is robust enough to withstand the conditions of a launch. The travelling wave tube meets all these requirements better than any other type of tube. Travelling wave tubes, in fact, have been used in all communications satellites launched so far—Telstar, Relay, and Syncom experiments—and will be used in the next generation of satellites, which it is hoped will lead to a world-wide commercial communication system.

The particular tube used in the Telstar experiment had the following characteristics [12]:

Centre frequency	4100 Mc/s
Maximum output power ..	4 watts
Helix voltage	1500 volts
Collector voltage	750 volts
Beam current	17·5 milliamperes
Heater power	1·4 watts
Bandwidth	200 Mc/s
Gain at 1 milliwatt input ..	36 db
Efficiency	37 per cent

The life of the tube has been estimated, on the basis of life tests on similar tubes and experience with tubes in service in terrestrial microwave relays, to exceed 10 years.

In missile and space-craft guidance

Some missiles and rockets are guided into their trajectories by information stored in them, others are guided from the ground until they disappear beyond the horizon. The latter method, called command guidance, has been successfully employed in hundreds of flights, including those of all communications satellites so far. It uses a missile-borne travelling wave tube as an amplifier of microwave signals sent up to it from the ground stations [3]. The ability to amplify signals over a wide frequency range, with a power gain of more than 20 000, and the ability to adjust the gain electronically over a wide range by varying the beam current, have led to the adoption of a travelling wave tube. A rocket undergoes enormous accelerations, shocks, and buffeting as it is launched through the atmosphere, and the travelling wave tube has to survive these. The necessary strength was achieved by making the focusing magnet and the tube as a unit held together by epoxy adhesive, the whole supported and encased by low-density foam plastic. Each tube was tested for one hour at vibrational frequencies varying from 50 to 2000 c/s and accelerations of 20 *g*. Its useful life is only a few minutes, of course, but much depends on it then in terms of costs, manpower, and effort spent.

References

[1] Kompfner, R. 'The Invention of the Travelling Wave Tube'. San Francisco Press, 1964

[2] 'British Television Relay Network'. *Elect. Commun.*, 29, 172, 1952.

[3] Apgar, W. D. and Bradford, C. E. *Bell Lab. Rec.*, 41, 19, 1963.

[4] Pierce, J. R. 'Traveling Wave Tubes'. Van Nostrand, New York. 1950.

[5] *Idem. J. appl. Phys.*, 11, 548, 1940.

[6] Wang, C. C. *Proc. Inst. Radio Engrs, N.Y.*, 38, 135, 1950.

[7] Brillouin, L. *Phys. Rev.*, 67, 260, 1945.

[8] Pierce, J. R. *J. appl. Phys.*, 24, 1247, 1953.

[9] Mendel, J. T., Quate, C. F., and Yocom, W. H. *Proc. Inst. Radio Engrs, N.Y.*, 42, 800, 1954.

[10] Laico, J. P., McDowell, H. L., and Moster, C. R. *Bell Syst. tech. J.*, 35, 1285, 1956.

[11] Jarrett, J. H. *West. Elec. Engr*, 5, 2, 1961.

[12] Bodmer, M. G., Laico, J. P., Olsen, E. G., and Ross, A. T. *Bell Syst. tech. J.*, 42, 1703, 1963.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Book reviews

Digitized by Arya Samaj Foundation Chennai and eGangotri

PHILOSOPHY OF SCIENCE

Traité de la méthode scientifique, *by R. Leclercq. Pp. viii+215. Dunod, Paris. 1964. 18F.*

The author's aim is to explain the basic processes of discovery and invention in science. Theory and practice cannot be strictly separated, and the road to scientific success is not paved by the stepping stones of formal logic alone. A 'heuristic' logic is needed; and this is mainly concerned with psychology.

The book begins with an historical account of the various methods that have been used in science. A chapter on the psychological method follows; various factors involved in scientific creativity are described. The logical method, which is interpreted as the schematization of practical procedures, is then discussed. The author proposes, tentatively, a mathematical formalism of scientific method; the chain of hypotheses leading to a scientific result is less rigid than the chain of deductive reasoning. Finally, cybernetics—the use of machines—is considered as a tool for research.

Today there is a world-wide interest, particularly among the managers of industry, in the problem of how to stimulate scientific creativity. M. Leclercq's book provides an interesting contribution towards the solution of this problem. *E. H. Hutten*

ASTRONOMY

Nebulae and Galaxies, *by Giorgio Abetti and Margherita Hack (translated from the Italian by V. Barocas). Pp. 264. Faber and Faber Ltd, London. 1964. 63s. net.*

Three-quarters of this book is concerned with the general properties of the local galaxy—our Milky Way system—and particularly with three different types of nebulae which are prominent in it. These are the planetary nebulae, and the irregular bright and dark nebulae. The extensive section on the first of these types gives a good idea of the complexity and variation of these objects, and of the evolutionary relationship between the nebula and the central star which is visible in many of them. The distinction between these and the irregular nebulae is clearly drawn, the latter being clouds of interstellar hydrogen gas, the former being visible because of the ionization occasioned by the presence of hot stars. The chapter on the properties of the galaxy deals with the Hertzsprung-Russell diagram and the probable evolutionary track of the various types of stars. The last two chapters on the extragalactic nebulae and the origin and evolution of the universe deal too briefly with subjects that have assumed great interest and importance in recent years. This edition is the translation of the Italian version which appeared in 1959. Five years is a long time in this phase of development of the subject, but parts of it remain of great value to students of astronomy. *A. C. B. Lovell*

HIGH-ENERGY PHYSICS

Strong Interactions and High Energy Physics, *edited by R. G. Moorhouse. Pp. xvi+475. Oliver and Boyd Ltd, Edinburgh and London. 1964. £5 15s. net.*

This book contains the lectures that were presented at the fourth Scottish Universities' Summer School in Physics held near Edinburgh during the summer of 1963. It maintains the high standard set in previous years. The school was attended by research graduates with at least one year's training in high-energy physics, and the subject matter is suitable for such an advanced audience. At the same time, the lectures are designed to cover the subject of the title in a comprehensive manner. It is therefore very valuable reading for any research student starting work in this field.

The lectures include among others an introduction to relativistic S-matrix theory by Squires; an excellent discussion of complex angular momentum by Oehme; and extensive discussions of phenomenological applications by Udgaonkar, Fubini, and Hamilton. An interesting new approach to three-particle systems by Lovelace provides a lively finale. *P. T. Matthews*

THERMAL PHYSICS

Thermal Physics, *by Philip M. Morse (third edition). Pp. xiii+455. W. A. Benjamin Inc., New York and Amsterdam. 1964. $10.50.*

This book is based on one of the three main courses required of seniors majoring in physics at the Massachusetts Institute of Technology. It deals with thermodynamics, kinetic theory, and statistical mechanics. The title is somewhat misleading, for the treatment of experimental work is perfunctory, and the casual schematic diagrams in which the results of long series of searching experimental investigations are sometimes given are in striking contrast to the elaborate detail with which the relevant theory is described. Moreover, the fact that there is only an occasional passing reference to the historical course of development has weighted the presentation heavily to the side of formal theory.

The logical structure of the theoretical schemes, at various levels of generality, and many particular matters, such as the statistical ensembles, are dealt with very thoroughly and with no evasion of difficulties. Working through the book would, however, be a very demanding and time-consuming struggle for a physicist seeking entry into the field, for the main paths have been obscured by a jungle of detail. In spite of the drawbacks of the book as a general text, there is little doubt that it will be well adapted to the overall context of studies at M.I.T. and there is much in it which will be helpful to those concerned with the presentation of the field at an advanced university level elsewhere. *E. C. Stoner*

FLAME PROCESSES

Nonsteady Flame Propagation, *edited by George H. Markstein. Pp. x+328. Pergamon Press, Oxford. 1964. £5 10s. net.*

The recent impetus given to quantitative study of the propagation, stability, and kinetic processes of flames has led to an activity so intense that any new worker is faced with a gap in available knowledge caused often by uncorrelated published work and also by the proliferation of technical reports. This situation has been partially rectified of late by the welcome appearance of a number of books and summaries, and this volume makes the most recent, and a most important, addition. It is both different and refreshing: different because it deals with non-steady flame phenomena arising from gaseous fuels—properties that are of direct interest to the aeronautical engineer; refreshing because much of its material will appeal to the flame kineticist as well.

The book is composed of contributions from three well-known authors. G. H. Markstein reviews the problems involved in flame propagation theory, discusses in detail a linearized perturbation treatment, and illustrates the phenomenon of flame front instability; H. Guenoche describes the theory and practice of flame propagation in tubes and closed vessels; and A. A. Putnam illustrates flame instability, oscillation, and noise. It seems regrettable that detonation phenomena could not have been included, and that there is also some duplication of material. However, this duplication can be welcomed in a field where the need has been for a summary of previous work, and even more for a review of the outstanding problems. The authors are to be congratulated for having tackled both aspects. *P. J. Padley*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

DIELECTRIC BREAKDOWN

The Theory of Dielectric Breakdown of Solids, *by J. J. O'Dwyer. Pp. viii+143. Clarendon Press: Oxford University Press. 1964. 30s. net.*

Dielectric breakdown is a complicated and difficult subject with many facets. This book is concerned with the more academic aspects. In part I, an account is given of the principal electronic theories of electric strength which have evolved since about 1930. Quite reasonably, because the distinction between impulse thermal breakdown and intrinsic breakdown is narrow, a conventional account is included of the well-established theory of thermal breakdown. This part of the book is at post-graduate level. The theoretical work is given in some detail, the material being well presented and the salient features of the various theories being clearly brought out. Active workers in the field, and insulation engineers who wish to obtain a background of fundamental knowledge, will find this part of the book extremely valuable.

Part II is entitled 'Applications', and in it experimental work is reviewed in the light of the various theories. Interest is concentrated mainly on the alkali halides, but some work on glass and polymers is included. The author's opinion is that little hope exists of understanding the breakdown process in more complex substances while it remains obscure in the simple ones. The reader will therefore be surprised to discover no mention of the work done in recent years on the breakdown of Si and Ge, which in many respects form better subjects of experiment than do the alkali halides. The review is very superficial, and no understanding is shown of possible consequences of the appreciable experimental difficulties. There are a number of misquotations and not all of the evidence available is quoted on some topics. The serious student must still assess the situation by reference to original papers and review articles.

R. Cooper

ELECTRON MICROSCOPY

Modern Developments in Electron Microscopy, *edited by Benjamin M. Siegel. Pp. xiii+432. Academic Press, New York and London. 1964. 96s. 6d. net.*

The volume includes two outstanding reviews for which many biologists will be grateful. D. W. Fawcett writes on electron microscopy in histology and cytology. He critically evaluates recent literature and draws with authority a clear picture of the cell and its organelles. Edward Kellenberger and Antoinette Ryter are equally excellent in describing bacteria. Both reviews have much of general interest.

As readable, but more specialized, is D. W. Pashley's account of developments in crystal physics. C. E. Hall contributes a short comment on biological macromolecules; here the microscope is not yet fully exploited, but he suggests it can have a major role in molecular biology.

The editor aims to acquaint new workers with the best of recent work. He should succeed, for these articles are extensively illustrated with superb pictures, although Fawcett's, alas, do not state the magnification.

The volume starts with a good, if not obviously relevant, description of the physics of the microscope, by Benjamin M. Siegel. Unfortunately, his optimistic speculations about possible atomic resolution are based on doubtful theoretical levels of contrast.

The short section on techniques includes a notable article on ultramicrotomy by Keith R. Porter, one of the masters of the art, and here all, however experienced, who cut sections are sure to learn something.

R. C. Valentine

REACTION MECHANISMS

Inorganic Reaction Mechanisms: An Introduction, *by John O. Edwards. Pp. xii+190. W. A. Benjamin Inc., New York and Amsterdam. 1964. $7.*

This aspect of inorganic chemistry is one of the newest and consequently there are very few volumes devoted to it: most of these do not give a truly balanced picture of the whole field and they could scarcely be called introductory texts. It is particularly gratifying therefore to see this book.

The author strives to preserve a balance between a survey of types of reactant species and their mechanisms, and a treatment suitably deep for an introductory account. The first three chapters are intended for the neophyte in mechanistic affairs and deal with such items as transition state theory; order and mechanism; binding strength and reaction rates; acids, bases, and solvents; and linear free-energy relationships. The next six chapters cover nucleophilic displacements; non-radical mechanisms for peroxide reactions; replacements in octahedral complexes; electron transfer reactions of complexes; reactions of oxyanions; and free radical reactions. The book concludes with a survey of unsolved problems.

The author has succeeded in the difficult task of selection for an introduction to a fast-advancing area of inorganic chemistry. If the reader wishes to delve deeper, there are key references at the end of each chapter: this is one of the book's most valuable features. It will be of value to third-year undergraduates, to research students, and to all those whose concern is with reaction mechanisms generally.

R. H. Prince

Fast Reactions in Solution, *by E. F. Caldin. Pp. x+306. Blackwell Scientific Publications, Oxford. 1964. 45s. net.*

Dr Caldin's book gives us for the first time a survey of the methods that we now have for following the course of fast chemical reactions in solution—reactions that are important in such diverse fields as inorganic chemistry and biology.

A general introduction sets the historical background, and surveys half-times accessible by the various methods; the energetics of very fast reactions; and the theory of rate constants of diffusion-controlled reactions. The methods are then described in the succeeding chapters. The simpler methods (such as the use of low concentrations; measurement of equilibrium constant and reverse reaction rate; and use of low temperatures) are considered first. Then follow chapters on flow methods; relaxation methods such as temperature-jump, pressure-jump, and electric impulse methods; relaxation methods of the kind exemplified by ultrasonic absorption, flash photolysis; photochemical, fluorescence, and electrochemical methods; electron spin resonance and nuclear magnetic resonance. The book closes with an excellent account of general topics (so difficult to find collated in the average kinetics text) on the mechanisms and energetics of reactions in solution.

Dr Caldin's survey is a most successful one: his treatment is brief but complete, to the point and generally stimulating. There are copious references to the literature.

R. H. Prince

ULTRAMICROANALYSIS

Inorganic Ultramicroanalysis, *by I. P. Alimarin and M. N. Petrikova (translated from the Russian by M. G. Hell). Pp. xv+151. Pergamon Press, Oxford. 1964. 40s. net.*

This monograph is a translation of the author's book published originally in Moscow in 1960; it contains references up to that date. It describes in sufficient detail for the uninitiated the techniques and apparatus for conducting chemical analyses of inorganic materials on the submicro scale. Attention is first given to the important and special features of ultramicroanalysis; this is followed by

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

descriptions of the apparatus required and the techniques to be adopted. These techniques are then applied to the qualitative analysis of various samples, emphasis being given to the preparation and solution of the materials to be examined. Finally, quantitative methods, necessitating a discussion of balances and weighing techniques, are described; the determinations involve either titrimetric or colorimetric procedures.

This little book is intended as an introduction to microgram experimentation, primarily for analytical chemists who are familiar with the basic chemical procedures as used on other scales of analysis but may not have encountered many of the techniques for ultramicroanalysis now described. The authors have made a judicious selection of the most reliable of the recognized techniques, and their long experience of the subject lends considerable authority to the text. It should prove of value to all interested in submicro methods of analysis. *W. I. Stephen*

POLYMERS

Encyclopedia of Polymer Science and Technology: Plastics, Resins, Rubbers, Fibers; *edited by Herman F. Mark, Norman G. Gaylord and Norbert M. Bikales. Vol. I, A–Amino Acids. Pp. xviii+893. Interscience Publishers, J. Wiley & Sons Inc., New York, London and Sydney. 1964. £15 net per volume for 12 volumes (2 per year); £18 15s. net for single volumes.*

The present work is the first of twelve volumes in which the editors plan to cover all facets of the science and technology of macromolecules, proposing to present some 450 articles written by specialists from all over the world. The volumes must certainly be regarded as a companion series to the Kirk-Othmer 'Encyclopedia of Chemical Technology' and will fulfil a similarly useful purpose. No fewer than 56 authors, of whom 43 are from industry in the United States, provide the material for this volume, and for some of the articles, a number of contributors collaborate to cover the theoretical and practical aspects of particular subjects.

There are authoritative and comprehensive reviews on many important items and in each are discussions on such issues as reactions, manufacture, properties, applications, hazards, analysis, testing, and statistics (these are taken mainly from sources in the United States). Extensive lists of useful and up to date references and many informative tables are included. The subjects covered include acrylic and methacrylic ester polymers, acrylonitrile polymers, adhesion and bonding, alkyd resins, and allyl polymers, while shorter articles deal with such items as abrasion resistance, acids, alcohols, amines, acrylic fibres, alfin catalysts, acrolein and aldehyde polymers, and—a sign of the times—ablative polymers and aerospace applications.

Naturally, the presentation, style and standard vary much according to the individual contributors. In general, they are of a high level, although here and there one encounters some vague statement or casually organized contribution. One feels too that the editors could have done more to eliminate some repetition between the various articles and to make the bibliography lists more readily accessible, instead of, in the case of composite reviews, including them at the end of each sub-section.

The book is well produced, printing and format are excellent, and the binding is such as to withstand the hard wear likely to be encountered. If the present volume is typical of the series, the editors will have largely succeeded in their task and provided a work of value to all who wish to obtain information on some aspect or other of macromolecules. We look forward to the next eleven volumes. *R. J. W. Reynolds*

MASS SPECTROSCOPY

Structure Elucidation of Natural Products by Mass Spectrometry, *Vol. I,* Alkaloids, *by Herbert Budzikiewicz, Carl Djerassi, and Dudley H. Williams. Pp. xi+233. Holden-Day Inc., San Francisco. 1964. $10.50.*

This is an excellent book. Both authors and publishers should be congratulated, both for the speed of production and the quality; the former, also, upon their coverage of a rapidly expanding field.

This book represents an effort of great value to other workers. It is an account of mass-spectrometric investigations into the main groups of alkaloids: indoles, iboga and voacanga compounds, tetrahydro-β-carbolines, eburnamine, aspidospermines, akuammicines, oxindoles, physostigmine, isoquinolines, emetine, colchicine, lycopodium, quinazoline, and others. A general introduction and some useful chemical reactions are included.

In spite of the complexity of the argument, there is only one infelicitous phrase, 'reasonable for two reasons' (p. 215), noticed by the reviewer. He does, however, find himself at variance with the authors on two points. The concept of a localized charge (p. 11) is an analytically useful pretence not in accord with the accepted view of the mobility of charge: this is not made clear. Also, there is some inconsistency in the treatment of individual compounds. The authors offer a different explanation for the production of the ion $m/e = 136$ in aspidospermatidine from that proposed in the original publication; on the other hand, the questionable composition of the ion $m/e = 225$ ($C_{14}H_{13}N_2O$) in ibogaine (p. 66) has passed without comment. *R. I. Reed*

MITOCHONDRION

The Mitochondrion, Molecular Basis of Structure and Function, *by Albert L. Lehninger. Pp. xx+263. W. A. Benjamin Inc., New York and Amsterdam. 1964. $9.90.*

During the last twenty years, the mitochondrion has advanced from the position of a doubtful cell inclusion to the status of one of the best documented of organelles. The change has been due in large measure to the work of Professor Lehninger and his associates. Here he first surveys the history of this development and the position of the mitochondria in intact cells, and then proceeds to an extended account of the biochemistry of mitochondrial processes and particularly of the respiratory oxidations and phosphorylations of which they are the site. It need hardly be said that this account is authoritative and up to date. There follows a similar account of ion-transport in mitochondria and of their energy-coupled changes of volume and structure. The correlation of function with ultrastructure is considered in its most recent developments and finally the still vexed questions of mitochondrial origins and growth with the associated syntheses. The cautious attitude of the author towards these problems shows clearly how much still remains to be done.

As a summing up at a fairly definite stage in the rapid development of mitochondrial studies, and as a stimulus and pointer to future progress, this book seems certain to become a lasting monument. *W. O. James*

PHYSIOLOGICAL EVOLUTION

Hormones and Evolution, *by E. J. W. Barrington. Pp. viii+154. The English Universities Press Ltd, London. 1964. 15s. net in U.K.*

The mechanisms and main pathways of morphological evolution are now well established and the subject commands a vast literature. Making sense of physiological evolution is a more difficult proposition, since the only clues we

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

have come from the physiology of contemporary animals, and the validity of deriving evolutionary patterns from such evidence is hard to assess. However, some progress has been made, and Professor Barrington reviews certain aspects of our present knowledge of hormones and endocrine systems of both vertebrates and invertebrates. The author, who is a practising comparative endocrinologist and an evolutionary biologist of great experience, is particularly well qualified to do this.

As might be expected, a good deal of attention is given to the thyroid and its hormones, but the steroids of gonads and inter-renals, and the protein and polypeptide hormones of the pituitary, are also treated in the light of their putative evolutionary history. The book, which is based on a series of lectures given in the University of London, contains much recent information from a very diverse literature. It is eminently readable and will be appreciated by a wide range of biologists. *J. M. Dodd*

DEVELOPMENT

Cellular Membranes in Development, *edited by Michael Locke. Pp. xvi+382. Academic Press, New York and London. 1964. 86s. net.*

This is an account of the 22nd Symposium for the Study of Development and Growth that took place in Storrs, Connecticut, in 1963. The title is somewhat misleading, since the emphasis in at least half of the ten papers is on the structure and physiology of cellular membranes rather than on developmental aspects. But these provide a good account of electron microscope studies of cellular membranes, together with consideration of the structure of the unit membrane, the similarity and continuity of the various membrane systems in the cell, cell contacts, and the formation of new membranes. There is, however, no discussion of the recent work suggesting a micellar structure for membranes. Papers on electron microscope studies of membranes in oocytes, growing roots, the fern egg, and fertilization, bring together much valuable information and one is struck by the dynamic nature of cellular membranes and the apparent rapidity with which they can form. It is clear that electron microscopy is not enough and there is an urgent need for data on the chemical nature and detailed molecular structure of cellular membranes. Lack of these data presents a formidable block to progress. Other approaches to cellular membranes are represented by papers on the permeability of the tonoplast and plasma membranes of growing plant cells, the properties of artificial lipid membranes, and the composition of bacterial cell walls. Steinberg has an excellent article in which he presents his views on the adhesive properties of the cell surface, and suggests that the sorting out of cells in aggregates is due to quantitative differences in adhesiveness.

The book can be recommended to all those interested in cell and developmental biology. *Lewis Wolpert*

BIOCHEMICAL TECHNIQUES

New Biochemical Separations, *edited by A. T. James and L. J. Morris. Pp. xi+423. D. Van Nostrand Co. Ltd, London. 1964. 84s. net.*

The editors intend this book to be used by research biochemists and chemists and also by students whose courses of study cover modern separational techniques. Out of seventeen chapters, five are concerned with gas-liquid chromatography of radioactive compounds, steroids, alkaloids, sugars, coenzyme A esters, bile acids, and amino acids. Thin-layer chromatography is prominent in a further eight chapters, which cover separations of amino acids, protein hydrolysates, alkaloids, steroids, triterpenoid compounds, bile acids, lipids, and proteins. The remaining four chapters deal with gel filtration (proteins, peptides, amino acids, and polysaccharides); the separation of polar lipids on silicic-acid-impregnated paper; and counter-current distribution of lipids.

There is at present no shortage of books on thin-layer chromatography or gas-liquid chromatography; and manufacturers of media for gel filtration supply copious literature on the uses of their products. However, the reviewer had no hesitation in adding this book to a well-stocked reference library. It is well-presented, clearly illustrated, and eminently readable. A book of this scope is needed to bridge the gap between the elementary, and often out of date, textbook and the over-detailed, and often insufficiently critical, annual reports. It is to be hoped that the editors will be able to produce other books on the same lines. *F. C. Happold*

NUCLEOHISTONES

The Nucleohistones, *edited by James Bonner and Paul Ts'o. Pp. xvii+398. Holden-Day Inc., San Francisco, London, and Amsterdam. 1964. $12.75.*

The convening of the first world conference on histone biology and chemistry reflects the recent renewed interest in the chemistry and biochemistry of nucleohistone. Much of the current work stems from the identification of deoxyribonucleic acid (DNA) as the central store of genetic information in the cell and the realization that, through the nucleohistone complex, histones may play a role in the regulation of DNA replication and the control of cell growth and differentiation.

The present volume, a collection of papers from that conference by many leading research workers in the field, serves well as an introduction and guide to what remains a complicated and somewhat confused subject. The contents include sections on the history, chemistry, structure, and metabolism of histones, together with discussions of the enzymology related to the nucleohistones and the role of histones in cell development. An optimistic note, suitably tempered with necessary caution, is struck throughout, and the difficulties due to the lack of knowledge as to the heterogeneity of isolated histones, and to the relative ignorance of their metabolism are given suitable prominence. *Richard Perham*

ENDOCRINOLOGY

Experimental Endocrinology, a Sourcebook of Basic Techniques, *by M. X. Zarrow, J. M. Yochim, J. L. McCarthy, and R. C. Sanborn. Pp. xvi+519. Academic Press, New York and London. 1964. 107s. 6d. net.*

As its title suggests, this is a students' book of well-known techniques used widely in endocrinology, although one could not find so many techniques used in a single laboratory anywhere in Britain. The book is concerned with the hormones and their assays. Thus there are chapters on oestrogens, progestogens, relaxin, androgens, epinephrin, and norepinephrin, adrenal corticoids, thyroid and the various pituitary hormones, parathormone, insulin and glucagon, and the hormones of the invertebrates. Each chapter begins with a description of the site of formation, chemical nature and action of the hormones, their biogenesis, metabolism and mechanism of action, and a general description of their methods of assay. There follows a series of numbered experiments describing the individual assay techniques. These are clear and concise and are supported by an excellent list of references. They cover the various methods of hypophysectomy, parabiosis, and other operative procedures, the reading of vaginal smears and numerous histological techniques, and a great variety of biochemical methods. Appendixes cover the care of laboratory animals, lists of hormones and their

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

actions, international standards, steroid structures and nomenclature, vehicles for administration of hormones, hormone solubilities, anaesthetics, various physiological fluids and culture media, and methods of numbering animals. There are excellent author and subject indexes. This is a valuable bench book for the laboratory concerned with methods of hormone assay. *A. C. Crooke*

BOTANY

The Living Plant, *by Alan J. Brook. Pp. ix+529. Edinburgh University Press, Edinburgh. 1964. 50s. net.*

At the present moment, two methods are fighting a battle for the control of the didactic approaches to biology. On one side is the 'logical' method of starting with the cell and building everything up from the common foundation, and on the other is the 'pedagogic' method of starting with the familiar and diverse—animals and plants—and eliciting the fundamental unities from study in developing depth.

This text may be considered a doughty blow for the latter approach. Its outlook is biological—that is to say structure and function are considered together from the start; and conventional, in that the fundamental physiological processes are treated in relation to the angiosperm. The other species are surveyed in much the usual way in the last third of the book.

Clarity, both in verbal description and in illustration, is a conspicuous merit in all parts of the book. Its method of production has allowed many of the admirably clear half-tones to be placed appropriately in the text with a minimal use of tiresome variations of paper. The unity achieved is symbolic of the author's intention for his subject and assists its successful achievement. An extensive glossary and index are also helpful. All this is admirable and has been achieved at a price which is not, by present standards, alarming. Dr Brook has produced a very welcome addition to the list of texts available for upper-school, and first-year university, students of botany. *W. O. James*

BOTANICAL PHYSICS

Physics in Botany, *by J. A. Richardson. Pp. ix+325. Sir Isaac Pitman & Sons, London. 1964. 42s. net.*

It is difficult to be enthusiastic about this book. As stated in the preface, its aim is to assist students to develop their knowledge of the important advances in botany which have been made possible by the application of the ideas and techniques of modern physics. In accordance with this aim there are chapters on electron microscopy and isotopes; but the reviewer could see no real point in including such topics as pH and plant growth, the movement of water and solutes in plants, or photosynthesis and respiration, subjects which are treated in the manner of an elementary text in plant physiology and no more. Added to these is a chapter on such a purely practical matter as controlled-environment growth rooms. As a result it is not at all clear for what readers the book is intended; it falls between at least three stools. On physical matters, particularly, its clarity often leaves much to be desired, as when 'quanta' are said to be 'integral multiples of $h\nu$' (p. 40) or the 'energy radiated' by a black body is given in the form $E_{max} \alpha T^5$ (p. 39) which might easily be taken as an expression of Stefan's law (in which the index is, of course, 4). Some of the thermodynamics is quite misleading (as on p. 211).

The main usefulness of the book may be to show interested sixth-formers that the range of topics covered by present-day botany is wider than they supposed. *D. C. Spanner*

PLANT GENETICS

Genetical Principles and Plant Breeding, *by Watkin Williams. Pp. x+504. Blackwell Scientific Publications, Oxford. 1964. 70s. net.*

This presentation of the principles of genetics which are relevant to plant breeding is also designed to provide an understanding of plant genetics for 'all trained biologists'. Although some of the recent advances in microbial genetics are mentioned, the basic principles are presented clearly with interesting examples from higher plants. One consequence of the dual objective is that the contents and arrangement of some chapters may not satisfy all readers. Detailed accounts of the mechanisms of breeding systems and of the nature of resistance to disease may be considered to be unnecessary supplements to accounts of the genetic basis and significance of these phenomena. Special techniques in plant breeding, such as the induction of polyploidy and of mutations, which are presented in a supplementary chapter, could be used to exemplify the contributions and limitations of these sources of genetic variation. There are interesting chapters on the adaptation of populations and on the effects and efficiency of selection. Professor Williams has written a useful and readable book. It is different from the rest of the increasing number of textbooks of genetics, and should certainly be used by many students of biology as well as by those studying agriculture. *J. K. Jones*

MYCOLOGY

Synchytrium, *by John S. Karling. Pp. xviii+470. Academic Press, New York and London. 1964. 125s. net.*

The jacket of this monograph claims that it is complete and presents all data and information relevant to the identification, classification, and phylogeny of species of *Synchytrium*. The book amply substantiates this ambitious claim. It is directed at post-graduate and research students—a designation which includes anyone who has graduated in mycology, however long ago. There is sufficient material in the book to satisfy most requirements.

Life cycles and development of species are described lucidly and illustrated by many excellent line drawings. Cytology and sexuality are surveyed and illustrated by negative line drawings. There is no serious loss of clarity, but the switch from one method of presentation to another serves no useful purpose. A chapter on host reactions summarizes current knowledge of the response of host plants to infection, with inevitable emphasis on interactions between *S. endobioticum* and *Solanum*. After discussion of the taxonomic criteria which have been applied in the past, descriptions of the genus, sub-genera, and species are presented; about three-quarters of the book is devoted to this section. A short chapter on geographical distribution of species, a comprehensive host index together with an extensive list of references, and a bibliography devoted to *Synchytrium endobioticum* complete an extremely useful addition to mycological literature. *F. Blackburn*

PHARMACOLOGY

Annual Review of Pharmacology, *Vol. IV, edited by Windsor C. Cutting. Pp. xxxii+453. Annual Reviews Inc., Palo Alto, California. 1964. $9.*

This volume maintains the high tradition set by the preceding reviews. Most of the contributors have succeeded in producing reviews that are stimulating as well as critical. For the first time, there is an article on receptor mechanisms, by R. F. Furchgott; this contains timely discussions of the new interpretations recently proposed by Paton and of attempts made by several workers, including Chagas, Waser, and Paton, to establish the situation and quantity of

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

one of the more elusive receptors. Other reviews of wide interest are on the biochemical mechanism of drug action, by J. R. Cooper; on modern concepts in the relationship between structure and biological activity, by F. N. Fastier; and on mechanisms of drug absorption and excretion, by Ruth R. Levine and E. W. Pelikan.

Eleanor Zaimis has contributed an excellent account of the pharmacology of the autonomic nervous system; its experimental investigation has had an extra stimulus through the controversy set off by the Burn and Rand hypothesis. Articles dealing with other topical subjects include antibacterial chemotherapy; pharmacology of reproduction and fertility; effect of drugs on the central nervous system; effects of drugs on contractions of vertebrate smooth muscle; and kinins. The next international meeting of pharmacologists will be held in 1966 in Brazil. It is therefore appropriate that a South American, José Ribeiro do Valle, should review hormones and related substances; and that another review, by J. H. Welsh, should be on the composition and mode of action of some invertebrate venoms which are being investigated intensively by South American pharmacologists. E. Rothlin has contributed a charming chapter of reminiscences and of experiences in his pharmacological career. The value of this volume is enhanced by its exhaustive indexes. *G. V. R. Born*

Introduction to Chemical Pharmacology, *by R. B. Barlow (second edition). Pp. viii+452. London: Methuen & Co. Ltd; New York: John Wiley & Sons Inc. 1964. £4 4s. net.*

A proper understanding of drug action can only be said to have been reached when this can be expressed in terms of molecular biochemistry, but unfortunately the complexity of the life processes occurring within the cells of any living tissue, together with inadequate knowledge of these processes, forms a barrier to progress. The systematic study of the action of drugs on living cells and tissues, however, frequently provides a means of extending our knowledge both of the living system itself and of the drug, since although the tissue cannot be strictly defined in chemical terms, the drug can be so defined, and, with certain assumptions, kinetic and other physicochemical principles may then be applied.

This work provides a carefully considered exposition of the physical and chemical principles of drug action. It has been completely re-written in the new edition, and considerably expanded in depth rather than breadth. In this, the author is to be congratulated, since although many important areas of practical pharmacology are omitted, these omissions are more than compensated for by the thoroughness of the treatment which the remainder has received. Thus, whilst it is disappointing to find that drugs acting on the central nervous system have been deliberately omitted and that there is no mention of steroid or peptide hormones, it is perhaps not too much to hope that the author will remedy these omissions in a companion volume at some later date. The present volume is confined, then, to a detailed treatment of drugs acting on the peripheral nervous system, and one example of a group of drugs acting directly on tissues rather than nerves—drug action at histamine receptors. Introductory chapters, concerned with the kinetics of drug receptor interaction and the principles of the quantitative experimental methods on which the kinetic studies rest, provide a unifying approach to a text which is both authoritative and easy to read. *J. B. Stenlake*

HISTORY OF SCIENCE

Anaxagoras and the Birth of Physics, *by Daniel E. Gershenson and Daniel A. Greenberg. Pp. xxv+538. Blaisdell Publishing Co., New York, London, and Toronto. 1964. $10.*

There is a real danger that the 'laymen and professional scientists' for whom this book is intended will take it as an authoritative exposition of the theory of Anaxagoras. Its 49 pages of essay, followed by 707 passages (translated) from ancient authors from the fourth century B.C. to the sixth century A.D., and 109 summaries of modern interpretations from 1687 to 1961, make an imposing structure. In a short review a full criticism is impossible, but such readers are entitled to be warned of its fundamental error.

(1) Owing to their ignorance of Aristotelian terminology, the writers have repeatedly misrepresented the information given by Aristotle about Anaxagoras's theory of matter. What Aristotle actually says is that Anaxagoras posited that what Aristotle called τὰ ὁμοιομερῆ (i.e. 'the uniform substances'), e.g. bone, flesh, marrow, etc., were elementary, simple substances. (The meaning of the term τὰ ὁμοιομερῆ is here irrelevant: in fact it means 'the things whose subdivisions bear the same name as the whole lump': thus, a bit of flesh is flesh, whereas a bit of an arm is not an arm.) In the writers' version, Aristotle is made to say that Anaxagoras holds that the fundamental constituents of matter are molecules of various substances like bone, etc.

(2) Anaxagoras also asserted (for a reason overlooked by the writers) that matter is infinitely divisible (not infinitely divided); and that in the beginning all matter existed as tiny pieces. These statements are mistaken by the writers for an assertion that the alleged 'molecules' are permanently infinitesimal in size, that is, that division into infinitely small particles is the permanent actual state of all matter. This is a complete travesty of Anaxagoras's theory, in which 'molecules' of a fixed size have no place. Anaxagoras has many claims on our admiration, but the propounding of a molecular theory of matter is not one of them. *A. L. Peck*

A History of Chemistry, *Vol. IV, by J. R. Partington. Pp. xxxii+1007. Macmillan & Co. Ltd, London; St Martin's Press, New York. 1964. £10 10s. net.*

This fourth volume of Professor Partington's encyclopædic four-volume history of chemistry deals with the development of chemistry during the nineteenth century and during part of the twentieth. With its 1000 pages it is larger by 150 and 200 pages than its predecessors, as might have been expected, and the price is twice that of the second volume, which perhaps might also have been expected. The arrangement of the material follows the pattern of the earlier volumes, being mostly assembled biographically with extensive bibliographical details. There are 91 illustrations, and excellent name and subject indexes. The first half of the volume (Part I) deals in a series of 17 chapters with electrochemistry from Galvani and Volta to Berzelius and with organic chemistry to the time of Kekulé, a chapter on atomic weights intervening. Part II (six chapters) describes physical chemistry from the earlier studies of chemical affinity to the rise of colloid chemistry; Part III (two chapters) is concerned with organic chemistry from Pasteur; Part IV (one chapter) with inorganic chemistry from Marignac and Stas; and Part V (one chapter) with radioactivity and atomic structure.

Douglas McKie

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

93

ENDEAVOUR

VOLUME XXIV SEPTEMBER 1965

Digitized by Arya Samaj Foundation Chennai and eGangotri

A review of the progress of science, published in five languages

Editor TREVOR I. WILLIAMS, M.A., B.Sc., D.Phil., F.R.I.C.
Foreign Editor G. N. J. BECK, B.Sc., A.M.I.E.E.
Assistant Editor W. A. OSMAN, B.Sc., M.Sc., A.R.C.S.

Contents

574.6(100)
118 Editorial: The International Biological Programme

539.126.6
119 Hypernuclei
R. Levi Setti, Dottore in Fisica

547.314:581.192.2
126 Polyacetylenic compounds in nature
A. W. Johnson, M.A., Sc.D., F.R.S.

561.26:582.263
131 Coccoliths
Maurice Black, M.A.

546.17.16
138 The fluorides of nitrogen
Charles B. Colburn, B.S., Ph.D.

656.021:519.24
143 Road traffic flow: some theories and their applications
A. J. Miller, M.Sc., Ph.D.

621.313.333
149 The search for a variable-speed induction motor
F. C. Williams, C.B.E., D.Sc., M.I.E.E., F.R.S., and J. F. Eastham, M.Sc., Ph.D.

582.263
155 Acetabularia
J. L. A. Brachet, M.D.

595.775:591.134
162 The rabbit flea and hormones
Miriam Rothschild

168 Book reviews

Some books received (cover iii)

Communications should be addressed to the Editor, Endeavour, South Block, Thames House, Millbank, London S.W.1 Telephone: Tate Gallery 2181

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

The International Biological Programme

The International Biological Programme (IBP), detailed plans of which have lately been published, stemmed from proposals that had been discussed by the International Council of Scientific Unions (ICSU) for several years. ICSU set up a planning committee in 1960 to see whether it would be desirable to establish a biological programme on an international basis and, if so, to draft a broad outline of it. The committee's report stated such a programme was not only desirable but urgent. As with the IGY, the organization of the IBP is independent of the participating governments, although most of the money required will come from them. The scheme is internationally as well as nationally supported, having the approval of UNESCO, FAO, and WHO.

In drafting the programme, it was recognized that though its general scope might be very wide, the number of objectives must be limited if it was to be manageable. ICSU therefore decided that the IBP should concern itself not with the whole of biology, but with 'the biological basis of productivity and human welfare'. Within this broad remit there were two main aims. One was to study, on a world-wide basis, organic production on the land, in fresh water, and in the seas: the potentialities of new, as well as of existing, resources were to be explored. The other was to study human adaptability to changing conditions. The first phase of this ambitious plan, devoted to design and feasibility studies and to methodology, has already started, and will last for two or three years.

There are seven sections of the IBP. These are devoted to the productivity of terrestrial communities; production processes; conservation of terrestrial communities; productivity of freshwater communities; productivity of marine communities; human adaptability; and the use and management of biological resources. It is relatively simple, and certainly valuable, to study natural resources as such, but the value of the work for future planning will be very limited if there is no study of the fundamental processes involved. The section that deals with plant growth on land will therefore co-ordinate fundamental studies of nitrogen fixation and photosynthesis; similarly, the section working on freshwater communities will study the role of bacteria in aquatic ecosystems.

The section working on the measurement of primary and secondary biological productivity of land communities will have to extend, to new areas of the world, research on such basic processes as energy flow, protein production, mineral cycling, and environmental pollution. There must also be a wide international co-operation between scientists of different disciplines. Great care will have to be taken to ensure that the communities studied represent significant major ecosystems.

The studies of secondary production will concentrate on the activities of the organisms that bring about decomposition and of the animals that live on the primary products. In these fields, intensive studies of specific populations or portions of food chains will clearly be more informative than any attempt to study the whole of a complex ecosystem.

The section on production processes will study the crucial processes upon which primary production depends. The most important of these are the nitrogen cycle, especially the biological fixation of nitrogen, and the utilization of solar energy.

The programme proposed for photosynthesis illustrates the approach that will be used throughout. It is important to evaluate overall photosynthetic activity—for example, to compare the productivities of different plant species—and this can be done at three levels. At the broadest level of field studies, techniques of growth analysis will be used that require only simple facilities and can therefore be undertaken in a large number of countries. A rather more detailed examination will involve experiments and computations requiring greater facilities and experience: these will be limited to a correspondingly smaller number of stations. Lastly, there will be experiments or field measurements that demand elaborate techniques and instrumentation; these will necessarily be confined to a very much smaller number of centres.

It was realized from the beginning that any world-wide study of biological processes would be handicapped if no sites were conserved so that they could be observed in their undisturbed state by future biologists. Among these sites, those on land are so important that a separate section was established to work on the conservation of terrestrial communities. This has set itself the task of establishing the scientific basis for a world programme of preserving areas of biological or physiographical importance. In this case the urgency is particularly great, because a delay may mean that the area is no longer worth preserving. This section has undertaken to establish an international record of objective data, with a view to using punched cards or magnetic tape for their evaluation.

Another section will study the productivity of freshwater communities. A good deal of research will be initiated, but here, as elsewhere in the programme, a major task is to support and co-ordinate existing work. Thus the productivity of fish-farms, and the transfer of material from land to sea by the rivers, are already being studied in many countries. Such work will be linked with that of the complementary section dealing with the productivity of marine communities.

The whole IBP is devoted to studying the relationships of living creatures to their environments, and it is therefore logical that one section should study human adaptability. The enormous rate of advance in technology that characterizes the present time will cause many communities that are at present changing only very slowly, or not at all, to be greatly altered in a short space of time. The effect of these changes on human biology must be studied, and the knowledge usefully applied. The section's plans range from a world survey of sample populations to intensive studies of selected groups. Some of the latter will include work on physiological fitness and on the nutritional demands of different habitats.

The seventh section will deal with the use and management of biological resources. Its aims are to study the genetic adaptation and variation of plants and animals, in order to find areas that can profitably be explored for additional germ-plasm material; to study little-used plants and new biological resources in general; to study biological control and plant diseases; and to investigate nutrition and food preservation.

The two years allowed for planning the IBP will be crucial ones, and will lay a heavy burden of responsibility on the organizers. Clearly, they must be at pains to ensure that all the projects finally approved are not only ones of high biological importance but ones for which an international effort is essential, for these are the criteria by which the programme will be judged as it develops.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Hypernuclei

Digitized by Arya Samaj Foundation Chennai and eGangotri

R. Levi Setti

The Λ-hyperon is a particle that occurs in cosmic radiation and in the radiation produced by high-energy accelerators. It can combine with a proton or a neutron in a normal nucleus, and, if it does so, it produces an unstable new particle called a hypernucleus. This article discusses the occurrence and properties of hypernuclei and the information about the forces acting between the Λ-hyperon and the proton or neutron that can be gained from studying them.

The atomic nucleus consists of protons and neutrons—nucleons—and the interactions between these bodies are the strongest that are known in nature; modern nuclear physics arose as an attempt to understand the nature of these strong interactions. H. Yukawa suggested in 1935 that the interactions could be understood in terms of the exchange between the nucleons of another particle, which he called the meson because its mass was intermediate between that of an electron and a nucleon. These mesons could be charged, either positively or negatively, or they could be neutral. The electromagnetic interactions that any charges produce are said to be medium strong interactions, but, like the electromagnetic interactions between the other charged particles of the atom, they are so weak in comparison to the force between nucleons that they have very little importance for the stability of the nucleus. The mesons—they are now called π-mesons—were actually discovered in cosmic radiation in 1947; they are known as π^+, π^-, and π^0, the superscripts indicating their charge. Since then, a number of other particles have been found in cosmic radiation and among the secondary particles produced by accelerators, and it has been found that they can be divided into three groups: the leptons, whose mass is small compared with that of the neutron; the baryons, with masses approximately equal to that of the proton; and the mesons, of intermediate mass. In this article we are particularly concerned with the mesons and the baryons. All of these particles, except the proton, are unstable, and their decays are said to be the result of weak interactions, as the forces involved are so much weaker than either of the other forces that have been mentioned. One of the reasons for studying the new particles is that their interactions are almost certainly related to those of the nucleons.

The baryons can be subdivided into the nucleons and the hyperons (table 1). The hyperons are all slightly more massive than the proton or the neutron, and they all decay at such a rate that their mean lifetime is about 10^{-10} seconds. They all react with the nucleons strongly, but only a limited number of reactions is allowed, by very particular conservation laws. Such reactions are indicated in table 1, where it is seen that in some cases the initial partners cannot transform into different final ones. Thus, for example, a Λ^0-hyperon is 'stable' in the presence of both protons and neutrons. In these conditions, binding between the hyperon and the nucleons may occur. The time needed for the strong reaction to operate between elementary particles so as to produce binding between them is about 10^{-24} seconds, so that if Λ^0 hyperons are produced in the presence of protons and neutrons, as an atomic nucleus, for example, they may form compound systems, hypernuclei. These are stable, in that their lifetime, again about 10^{-10} seconds, is very much longer than the time needed for their formation. Although several other hyperons could bind to either protons or neutrons, the only hypernuclei that have been observed are derived from the Λ^0-hyperon, Λ for short. They can be detected by their traces in nuclear photographic emulsion or in a bubble chamber; the hypernucleus will produce a track leading from a 'star' that records its formation to another one recording its spontaneous decomposition (figure 1). They are prepared inside the detector by exposing it to cosmic rays or to the high-energy beam of an accelerator. Hypernuclei are designated by the chemical symbol of the nucleus with which the Λ-hyperon is associated; a superscript showing the total mass; and the subscript Λ. Thus ${}_{\Lambda}H^3$ is a system composed of a H^2 nucleus bound to a Λ-hyperon.

The first hyperfragment was discovered by M. Danysz and J. Pniewski in 1952 [1]. The source of the high-energy particles in this case was cosmic radiation, and the detector was nuclear emulsion carried to a high altitude by means of a free balloon. The example shown in figure 1 was the first to be ascribed to a specific hypernucleus, ${}_{\Lambda}H^3$ in this case [2]. The picture shows a typical high-energy nuclear disintegration (star S), and a track originating from it and terminating in a secondary small star (S'). The particles that are ejected at S' travel in opposite directions. One leads to a third star, S'', characteristic of the capture of a π^--meson, the other is a heavy, short recoil-particle. The decay products travel in opposite directions along the same line. This suggests that there are only two decay products, recoiling from one another. The distance the π^--meson travelled gave a measure of its energy, and therefore of its linear momentum. The recoil particle must have the same linear momentum. The distance it travelled established it uniquely as an He^3 nucleus. Thus the hypernucleus decay scheme was

$$ {}_{\Lambda}H^3 \rightarrow \pi^- + He^3 + 41 \text{ MeV} \qquad \ldots . (1) $$

The Λ-hyperon had two decay products ($\Lambda \rightarrow p + \pi^-$), but only the π^- emerged as a free particle. The proton was bound to the H^2 hypernuclear core, as an He^3 nucleus. The energy balance in this decay reaction gave a measure of the energy, B_{Λ}, binding the Λ-hyperon to the H^2 in ${}_{\Lambda}H^3$. This is one of the more revealing parameters in understanding the structure of hypernuclei.

R. Levi Setti, *Dottore in Fisica*
Was born in Milan, Italy, in 1927, and educated at the University of Pavia. He then joined the University of Milan, where he began research in elementary particle physics. Since 1956 he has shared a joint appointment with the Enrico Fermi Institute for Nuclear Studies and the Physics Department at the University of Chicago, where he is now a Full Professor. His research interests include studies of heavy mesons, hyperons, and hypernuclei.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Table I
Hyperon and nucleon properties

Symbol	Spin	Mass (MeV)	Mean life (sec)	Decay modes	Fast reactions with nucleons		Candidate for hypernuclear formation
p	1/2	938·2	Stable	—	$p+p\rightarrow p+n$	1	ordinary
					$p+n\rightarrow p+n$	2	nuclear
n	1/2	939·5	$1{\cdot}0\times10^{3}$	$p+e^{-}+\nu$	$n+p\rightarrow n+p$	3	constituents
					$n+n\rightarrow n+n$	4	
Λ	1/2	1115·4	$2{\cdot}6\times10^{-10}$	$p+\pi^{-}$	$\Lambda+p\rightarrow\Lambda+p$	5	Yes
				$n+\pi^{0}$	$\Lambda+n\rightarrow\Lambda+n$	6	Yes
Σ^{+}	1/2	1189·4	$0{\cdot}8\times10^{-10}$	$p+\pi^{0}$	$\Sigma^{+}+p\rightarrow\Sigma^{+}+p$	7	Yes
				$n+\pi^{+}$	$\Sigma^{+}+n\rightarrow\Lambda+p$	8	No
Σ^{0}	1/2	1192·3	$<1{\cdot}0\times10^{-14}$	$\Lambda+\gamma$	$\Sigma^{0}+p\rightarrow\Lambda^{0}+p$	9	No
					$\Sigma^{0}+n\rightarrow\Lambda^{0}+n$	10	No
Σ^{-}	1/2	1197·1	$1{\cdot}6\times10^{-10}$	$n+\pi^{-}$	$\Sigma^{-}+p\rightarrow\Lambda^{0}+n$	11	No
					$\Sigma^{-}+n\rightarrow\Sigma^{-}+n$	12	Yes
Ξ^{0}	1/2	1314·3	$3{\cdot}1\times10^{-10}$	$\Lambda+\pi^{0}$	$\Xi^{0}+p\rightarrow\Xi^{0}+p$	13	Yes
					$\Xi^{0}+n\rightarrow\Lambda+\Lambda$	14	No
Ξ^{-}	1/2	1320·8	$1{\cdot}7\times10^{-10}$	$\Lambda+\pi^{-}$	$\Xi^{-}+p\rightarrow\Lambda+\Lambda$	15	No
					$\Xi^{-}+n\rightarrow\Xi^{-}+n$	16	Yes
Ω^{-}	3/2	1675	$\sim0{\cdot}7\times10^{-10}$	$\Xi^{-}+\pi^{0}$	$\Omega^{-}+p\rightarrow\Xi^{0}+\Lambda$	17	No
				$\Xi^{0}+\pi^{-}$	$\Omega^{-}+n\rightarrow\Xi^{-}+\Lambda$	18	No
				$\Lambda+K^{-}$			

Let us consider a ${}_{\Lambda}H^{3}$ hypernucleus formed as follows:

$$H^{2}+\Lambda={}_{\Lambda}H^{3}+B_{\Lambda} \qquad \ldots.(2)$$

B_{Λ} is the energy that is liberated when a Λ hyperon falls from the energy level of the unbound system, $H^{2}+\Lambda$, to the level of the bound system ${}_{\Lambda}H^{3}$. It has therefore the same value as the energy needed to separate the Λ hyperon in ${}_{\Lambda}H^{3}$ from its 'core' H^{2}. The masses of the particles on the left-hand side of equation (2) are well known, and the mass of ${}_{\Lambda}H^{3}$ is also known, from reaction (1). Thus,

$$B_{\Lambda}=H^{2}+\Lambda-\pi^{-}-He^{3}-4{\cdot}1\simeq2\text{MeV} \qquad \ldots.(3)$$

where the symbols stand for the masses of the particles, measured in MeV. This example shows how hypernuclei are identified and values of B_{Λ} determined. Nowadays, the approach is in essence the same, although electronic computers are applied to the observed ranges and emission angles of the particles to find the particular permutation of decay products that will satisfy the demands for the conservation of momentum and energy.

Another example of a complete sequence of hypernuclear production and decay is shown in figure 2 [3]. Here a K^{-}-meson, produced by the Berkeley Bevatron, slows down and is captured by a nucleus of the detector at A. A short hypernuclear track F leads to point B, where the hypernucleus disintegrates. Its decay products are a π^{-}-meson, a proton, and a particle with a short recoil. This last in turn decays in a very characteristic fashion by first emitting an electron, and then two He^{4} nuclei. The event represents the production of a ${}_{\Lambda}Li^{9}$ hypernucleus, which then decays:

$$\begin{array}{c} {}_{\Lambda}Li^{9}\rightarrow\pi^{-}+p+Li^{8}+29{\cdot}6\text{ MeV} \\ \downarrow \\ e^{-}+\bar{\nu}+Be^{8} \\ \downarrow \\ He^{4}+He^{4} \end{array} \qquad \ldots.(4)$$

In this type of decay, both Λ-decay products, p and π^{-}, are directly visible, and the associated nucleus of Li^{8} recoils.

A perhaps more spectacular, although less informative, event is depicted in figure 3. In this case, a nucleus of silver or bromine is violently disrupted at A by a very energetic (1·5 GeV/c) K^{-}-meson from the CERN proton-synchrotron. The nucleus loses energy, by emission of several nuclear fragments, and then recoils as a heavy hypernucleus, carrying the Λ-hyperon within. In this case, the Λ-hyperon itself transforms in a reaction with a nucleon in the host hypernucleus, and several particles of the latter are emitted at point B.

If the hypernucleus decays to eject a π^{-}-meson—the decay is called a mesonic decay—the hypernucleus involved can generally be identified. Furthermore, the energy balance for such events can be established, in individual cases, to an accuracy of $\sim0{\cdot}5$ MeV. (A large fraction of the available energy is, in fact, carried away by the rest-mass of the π^{-}-meson, 139·6 MeV.)

In a non-mesonic decay (figure 3), neutrons are frequently emitted, and this usually makes it impossible to identify the hypernucleus. In addition, the kinetic energy release is greater, by the rest mass of the π^{-}-meson, than in mesonic decays. The binding energy therefore cannot be accurately measured. The information on hypernuclei presented in the rest of this article will be based mainly on the analysis of mesonic decays.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

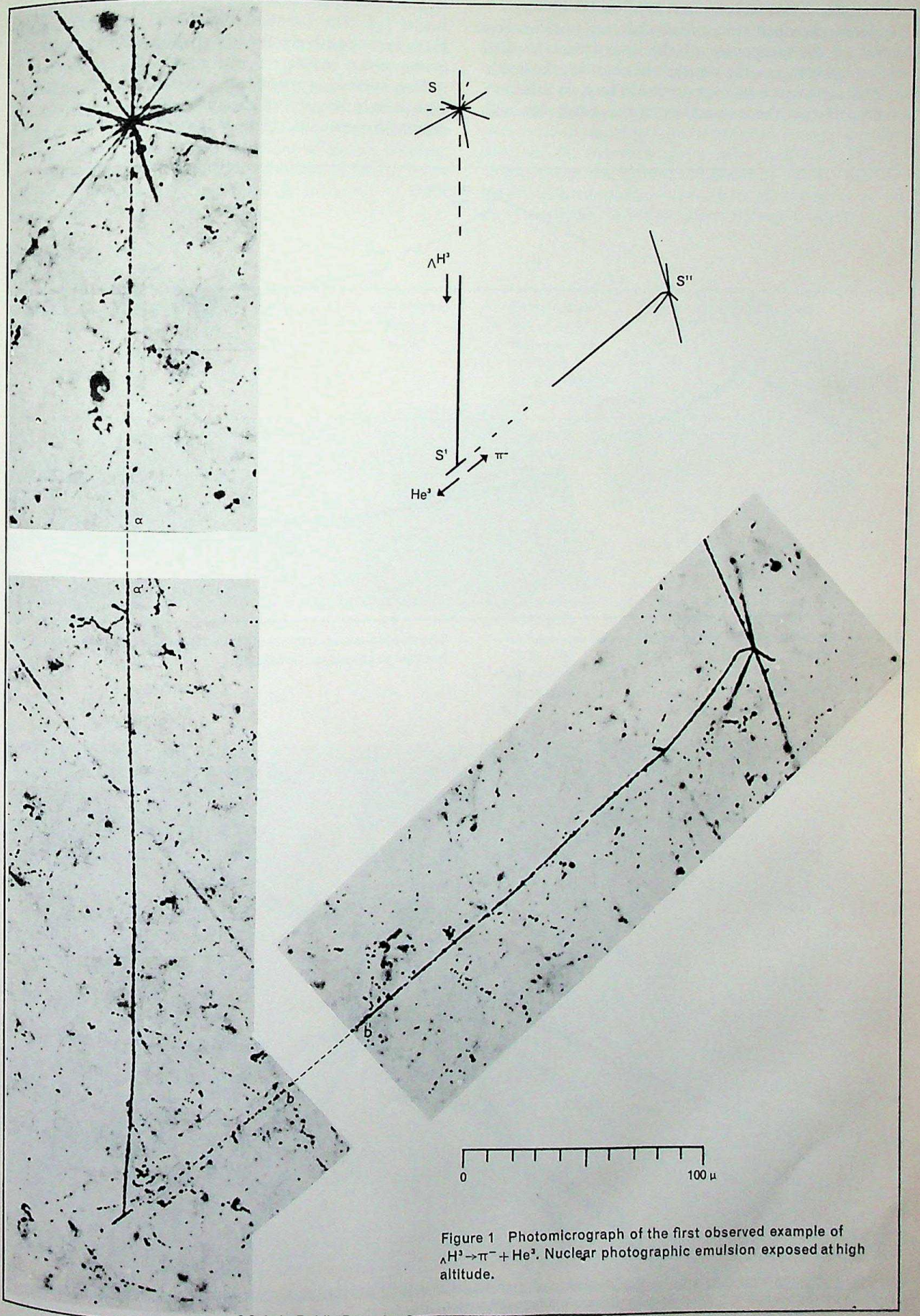


Figure 1 Photomicrograph of the first observed example of $_{\Lambda}H^{3} \rightarrow \pi^{-} + He^{3}$. Nuclear photographic emulsion exposed at high altitude.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Hypernuclear systematics and Λ-binding energies

The occurrence and structure of ordinary nuclei reflect several of the properties of the interaction of their isolated constituents, the proton and neutron; the occurrence and structure of hypernuclei reflect, in addition, the properties of the interactions of the Λ-hyperon with nucleons.

Table 11 shows the salient features of the light hypernuclei [4]. The tabulation includes all species which have been positively identified, and also those whose existence can be inferred with reasonable certainty.

One interesting point is that the table stops at ${}_{\Lambda}N^{14}$. This is only because of the difficulty of identifying the heavier hypernuclei. Hypernuclei of mass up to ~100

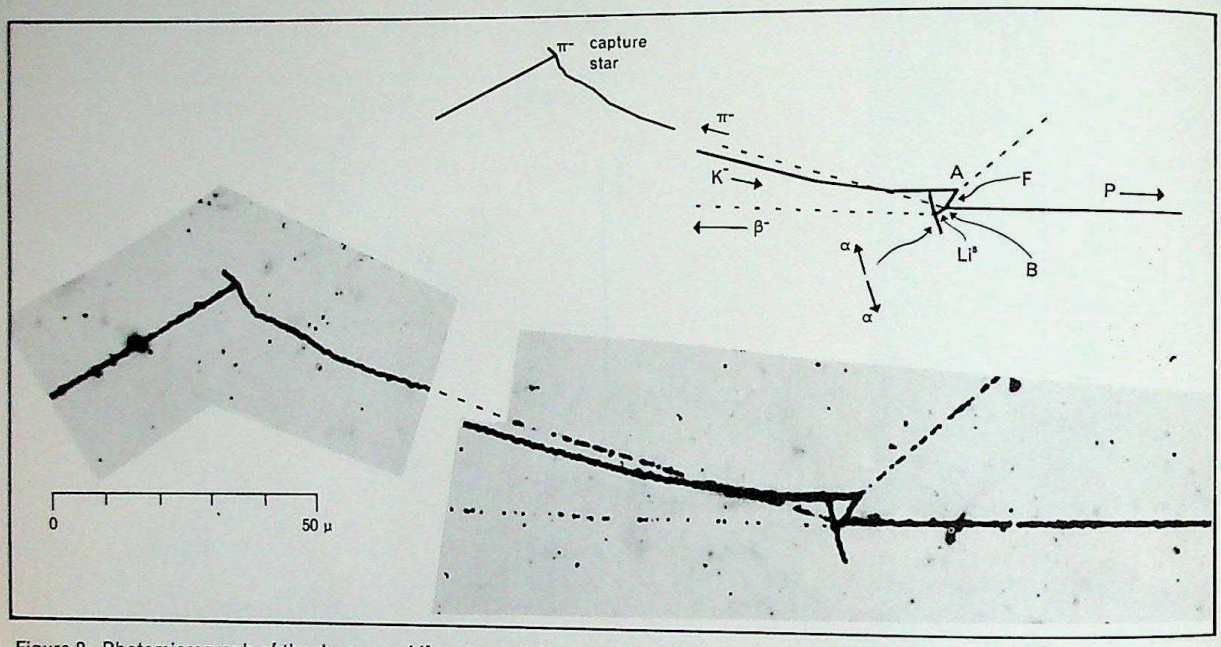


Figure 2 Photomicrograph of the decay ${}_{\Lambda}Li^{9} \rightarrow \pi^{-} + p + Li^{9}$, $Li^{9} \rightarrow e^{-} + \bar{\nu} + Be^{8*}$, $Be^{8*} \rightarrow 2He^{4}$. The hypernucleus originates from the capture of a K^{-}-meson in nuclear photographic emulsion.

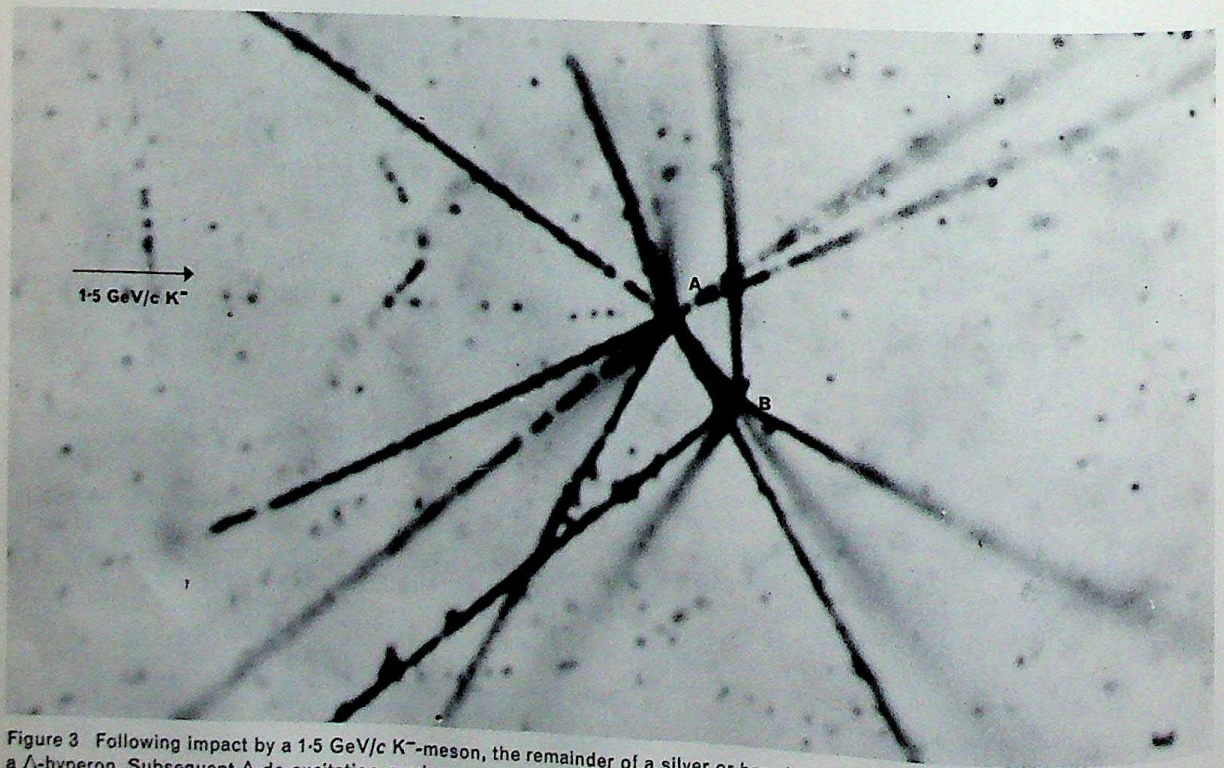


Figure 3 Following impact by a 1·5 GeV/c K^{-}-meson, the remainder of a silver or bromine nucleus recoils after trapping a Λ-hyperon. Subsequent Λ-de-excitation produces a secondary star.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

are known to exist, although they have never been exactly identified.

A second interesting point is that the lightest possible hypernucleus, ${}_{\Lambda}H^{2}$, is not included. This would correspond to the bound system of a Λ-hyperon with a proton, but it has never been observed. This is because the strength of the attraction between a Λ-hyperon and a nucleon on its own is not sufficient to secure binding. As soon as the Λ-hyperon is in presence of two or more nucleons, the overall attraction is sufficient to form bound states.

The very existence of some species rather than others, and the energies with which the Λ-hyperons are bound, provide several clues to the character of the interaction between a Λ-hyperon and a nucleon. Table II shows groups of hypernuclei with the same mass but different charges. These are called charge multiplets and have a particular symmetry—the Λ-binding energy is almost identical for members of the same multiplet. In other words, the strong interaction between nuclear particles, extended here to the interactions of hyperons as well as of nucleons, is independent of the charges on the

Table II
Light Hypernuclei

Nuclear core	Hypernucleus	Spin J	Λ-binding energy (MeV)	Sample size No. of events N.E. = nuclear emulsion He B.C. = helium bubble chamber	Typical pionic decay modes
H^{2}	${}_{\Lambda}H^{3}$	1/2	0·3	> 50 N.E. > 50 He B.C.	$\pi^{-}+He^{3}$, $\pi^{-}+p+H^{2}$, $\pi^{-}+2p+n$
H^{3}	${}_{\Lambda}H^{4}$	0	2·0	>150 N.E. >150 He B.C.	$\pi^{-}+He^{4}$, $\pi^{-}+p+H^{3}$, $\pi^{-}+n+He^{3}$, $\pi^{-}+2H^{2}$, $\pi^{-}+p+n+H^{2}$
He^{3}	${}_{\Lambda}He^{4}$	0	2·3	> 60 N.E. >350 He B.C.	$\pi^{-}+p+He^{3}$, $\pi^{-}+2p+H^{2}$, $\pi^{-}+3p+n$, $\pi^{+}+n+H^{3}$, $\pi^{0}+He^{4}$
He^{4}	${}_{\Lambda}He^{5}$	(1/2)	3·1	>200 N.E.	$\pi^{-}+p+He^{4}$, $\pi^{-}+H^{2}+He^{3}$
He^{6}	${}_{\Lambda}He^{7}$	(1/2)	~4·9	~15 N.E.	$\pi^{-}+Li^{7}$, $\pi^{-}+p+He^{6}$, $\pi^{-}+H^{3}+He^{4}$, $\pi^{-}+n+H^{2}+He^{4}$
Li^{5}	${}_{\Lambda}Li^{7}$	(1/2)	5·5	~25 N.E.	$\pi^{-}+Be^{7}$, $\pi^{-}+p+Li^{6}$, $\pi^{-}+He^{3}+He^{4}$, $\pi^{-}+p+H^{2}+He^{4}$
Be^{6} (unbound)	${}_{\Lambda}Be^{7}$	(1/2)	~4·9	~2 N.E.	$\pi^{-}+3p+He^{4}$
Li^{7}	${}_{\Lambda}Li^{8}$	1	6·6	~50 N.E.	$\pi^{-}+2He^{4}$, $\pi^{-}+p+Li^{7}$
Be^{7}	${}_{\Lambda}Be^{8}$	(1)	6·4	~5 N.E.	$\pi^{-}+p+He^{3}+He^{4}$
Li^{8}	${}_{\Lambda}Li^{9}$	(3/2)	8·0	~10 N.E.	$\pi^{-}+Be^{9}$, $\pi^{-}+n+2He^{4}$
Be^{8} (unbound)	${}_{\Lambda}Be^{9}$	(1/2)	6·5	~10 N.E.	$\pi^{-}+p+2He^{4}$
(B^{8})	(${}_{\Lambda}B^{9}$)	(3/2)	(8)	*	($\pi^{-}+C^{9}$, $\pi^{-}+p+B^{8}$, etc.)
(Li^{9})	(${}_{\Lambda}Li^{10}$)	(1)	(~8·5)	*	($\pi^{-}+Be^{10}$, $\pi^{-}+p+Li^{9}$, etc.)
Be^{9}	${}_{\Lambda}Be^{10}$	(1)	~9·5	~5 N.E.	$\pi^{-}+B^{10}$, $\pi^{-}+He^{4}+Li^{6}$
B^{9}	${}_{\Lambda}B^{10}$	(1)	~10	~6 N.E.	$\pi^{-}+C^{10}$
(C^{9})	(${}_{\Lambda}C^{10}$)	(1)	(~8·5)	*	($\pi^{-}+2p+B^{8}$, $\pi^{-}+3p+He^{3}+He^{4}$, etc.)
(Be^{10})	(${}_{\Lambda}Be^{11}$)	(1/2)	(~8·5)	*	($\pi^{-}+B^{11}$, $\pi^{-}+He^{3}+Li^{8}$, $\pi^{-}+He^{4}+Li^{7}$, etc.)
B^{10}	${}_{\Lambda}B^{11}$	(5/2)	10	~5	$\pi^{-}+C^{11}$, $\pi^{-}+He^{3}+2He^{4}$
(C^{10})	(${}_{\Lambda}C^{11}$)	(1/2)	(~8·5)	*	($\pi^{-}+He^{3}+B^{8}$), etc.
(Be^{11})	(${}_{\Lambda}Be^{12}$)	(1)	(~9·5)	*	($\pi^{-}+B^{12}$, $\pi^{-}+He^{4}+Li^{8}$, etc.)
B^{11}	${}_{\Lambda}B^{12}$	(1)	10·5	~10	$\pi^{-}+3He^{4}$, ($\pi^{-}+C^{12}$)
(C^{11})	(${}_{\Lambda}C^{12}$)	(1)	(10·5)	*	($\pi^{-}+N^{12}$, $\pi^{-}+He^{4}+B^{8}$, etc.)
(N^{11})	(${}_{\Lambda}N^{12}$)	(1)	(~9·5)	*	($\pi^{-}+4p+2He^{4}$, etc.)
(B^{12})	(${}_{\Lambda}B^{13}$)	(3/2)	(~10·6)	*	($\pi^{-}+C^{13}$, $\pi^{-}+He^{4}+Be^{9}$, etc.)
C^{12}	${}_{\Lambda}C^{13}$	(1/2)	~10·6	~2	$\pi^{-}+N^{13}$, ($\pi^{-}+p+3He^{4}$)
(N^{12})	(${}_{\Lambda}N^{13}$)	(3/2)	(~10·6)	*	($\pi^{-}+p+He^{4}+B^{8}$, etc.)
C^{13}	${}_{\Lambda}C^{14}$	(1)	~13	~2	$\pi^{-}+N^{14}$, ($\pi^{-}+H^{2}+3He^{4}$)
N^{13}	${}_{\Lambda}N^{14}$	(1)	~12	~1	$\pi^{-}+O^{14}$, ($\pi^{-}+2p+3He^{4}$)

* Hypernucleus as yet unobserved, but which may reasonably be expected to exist.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

particles. One is familiar in ordinary nuclear physics with 'mirror nuclei'; these are pairs of nuclei having the same mass number, in which the number of protons of one member equals the number of neutrons of the other. Such mirror nuclei, ignoring small corrections due to the electromagnetic interactions among protons, have equal binding energies. This means that the interaction of p-p, p-n, n-n pairs is the same; it is independent of the electric charge of the interacting partners. Typical examples of mirror nuclei are H^3 and He^3, and Li^7 and Be^7. The independence has been directly observed in scattering experiments involving only two partners at a time.

As the Λ-neutron and Λ-proton interaction are also charge-independent, there are 'mirror-hypernuclei' that reflect the structure of the nuclear cores, and exhibit Λ-binding energies that are very nearly equal. These are shown in Table II; examples are ${}_{\Lambda}H^4$ and ${}_{\Lambda}He^4$, and ${}_{\Lambda}Li^8$ and ${}_{\Lambda}Be^8$. Considerations of this nature enabled R. H. Dalitz to predict the existence of ${}_{\Lambda}H^4$, ${}_{\Lambda}He^5$, and other species that have since been discovered. Several predicted species that have not yet been observed are indicated with an asterisk in table II. The observed small deviations in the binding energy of mirror hypernuclei are interpreted as due to particular effects of the electromagnetic interaction; this is, naturally, charge-dependent.

The Λ-binding energies increase steadily from a fraction of a MeV for the hypertriton to a value, close to saturation, of $\sim$25 MeV for hypernuclei in the region of $A \sim 100$, where A is the mass number of the core. Superimposed on this overall trend are variations of about 0·5–1·5 MeV.

The Pauli exclusion principle as applied to the nucleus says, in effect, that any energy level cannot be occupied by more than two neutrons or protons, and can accommodate these two only if their spins are anti-parallel. This restriction, and the spin-dependence of the nucleon-nucleon interaction, produce very dramatic variations in the energy with which the last neutrons of light elements are bound. Thus, for example, the neutron binding energy of the last neutron in He^4 is $\sim$20·5 MeV, while the binding energy of an additional neutron to He^4 is $-\sim$2 MeV. That is to say, He^5 appears only as a resonant state, at $\sim$2 MeV, between a neutron and He^4. The exclusion principle means that an additional neutron cannot go into the already filled s-shell; it would have to occupy a higher energy level in the vacant $p_{3/2}$ shell, and here the attraction to the He^4 core is insufficient to yield a bound state.

However, a Λ-hyperon can always occupy the lowest s-state, as long as not more than one other is present; a second Λ-hyperon can be accommodated in an s-state, with its spin antiparallel to the first. A third Λ-hyperon would have to go in a higher shell, the p-shell, for example. The exclusion principle applies, in fact, only to identical particles.

The energy of a Λ-bound state is thus determined primarily by the attraction due to the combined effects of all the nucleons—the nuclear potential well—and by the size of the hypernucleus. In fact, neglecting the fine effect due to the spin dependence of the Λ-nucleon interaction, the following relation holds approximately for heavy hypernuclei:

$$B_\Lambda = D_\Lambda - \frac{C}{A^{2/3}} \qquad \ldots(5)$$

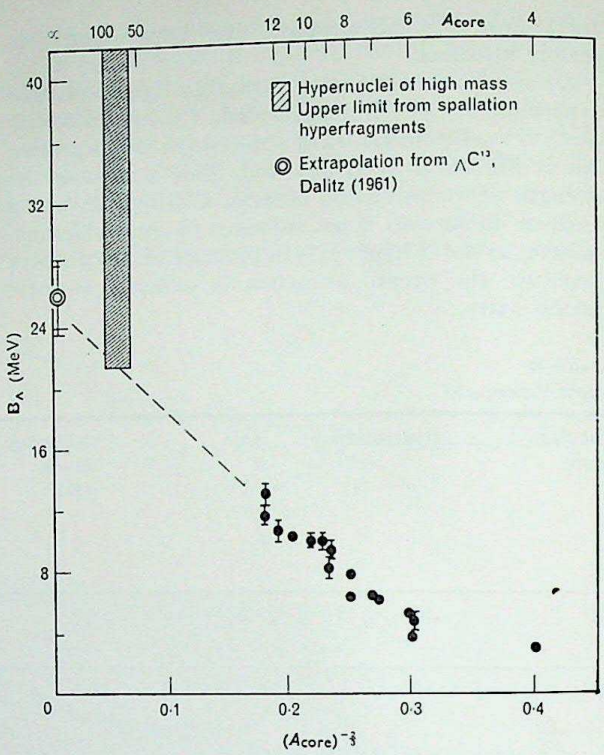


Figure 4 Λ-binding energies as a function of $(A_{core})^{-2/3}$. A linear extrapolation to the origin of the abcissa yields the depth D_Λ of the Λ-nuclear potential well.

where D_Λ is the depth of the nuclear potential well affecting the Λ-hyperon, and C is a constant. Thus a graph of B_Λ against $A^{-2/3}$ is approximately linear (figure 4). As $A \to \infty$ in equation (5), $B_\Lambda \to D_\Lambda$; that is, the depth of the Λ-nucleus potential well equals the Λ-binding energy in an infinitely massive hypernucleus. A linear extrapolation of the graph as $A^{-2/3} \to 0$ yields an estimate of the well-depth parameter D_Λ. This was used [5] to give an upper limit for the binding energy of the hyperfragments having a mass in the range 60–100.

The spins of hypernuclei

Some of the smaller differences in the Λ-binding energies observed between different isospin multiplets for hypernuclides are attributed to the spin dependence of the interaction between a Λ and a nucleon. Thus for ${}_{\Lambda}Li^7$, $B_\Lambda \sim 5{\cdot}5$ MeV, while for ${}_{\Lambda}He^7$ and ${}_{\Lambda}Be^7$, $B_\Lambda \sim 4{\cdot}9$ MeV; for ${}_{\Lambda}Be^9$ $B_\Lambda \sim 6{\cdot}5$ MeV, while for ${}_{\Lambda}Li^9$, $B_\Lambda \sim 8$ MeV.

The interaction between two nucleons is known to be spin-dependent. The attraction between a proton and a neutron, for example, is stronger when the two spins are parallel to each other than when they are antiparallel. In the first system, the deuteron is bound by 2·2 MeV; the second shows a repulsion of 70 keV.

Whether or not the Λ-nucleon interaction is also spin-dependent cannot be predicted *a priori*. The differences noted above could be explained in terms of an attraction between the Λ-hyperon and the nuclear core that depends on the spin of the core as a whole, as opposed to that of the nucleon with which the Λ-hyperon interacts. In fact, the nuclear core of ${}_{\Lambda}Li^7$, with the higher B_Λ, is Li^6, a nucleus of spin 1; the cores of ${}_{\Lambda}He^7$ and ${}_{\Lambda}Be^7$, with the lower B_Λ, have spin 0. Since, however, the spins of the hypernuclei in these cases are not known, it is not possible

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

to decide whether it is the spins of the nucleons or those of the cores that are responsible for the differences in the binding energies. It is, in some cases, possible to determine the spins of the hypernuclei, and this has shown that the favoured Λ-nucleon spin orientation, the one which is more attractive, is the antiparallel one, opposite to the situation for the nucleon-nucleon interactions. Thus, in table II, the hypernuclear spins indicated in parenthesis are those that are not experimentally determined, but that can be inferred because they give the lower energy for the ground state—the larger B_Λ. In most of the cases this corresponds to the spin of the core less the spin, 1/2, of the Λ-hyperon.

An outlook on hypernuclear physics

This introduction to the hypernuclei is limited to discussing those aspects that best illustrate some of the fundamental properties of the interaction between a nucleon and a Λ-hyperon. The study of hypernuclei yields a wealth of other information, reaching deeply into the properties of strange particles as well as of nuclear physics. It is remarkable in a way that so much could be learned from a very small sample of events, compared with the effort involved in learning about ordinary nuclei, which are present in molar quantities. In this sense, the Λ-hyperon, due to its instability, has shown itself as an invaluable probe.

While the main features of the strong interaction of the Λ-hyperon have been explored, much remains to be learned about the systematics of hypernuclear species, about the weak interaction properties of the Λ-hyperon, and about various processes where ordinary nuclear physics plays the dominant role. A glance at table II shows how much could be added to it. Several species have not been observed at all, and many are known to exist only on the basis of a few individual examples. The spins of only three or four hypernuclei have been experimentally determined. Hypernuclear excited states are expected to exist, but large samples of events will be necessary for their identification.

One would also like to know the lifetimes of the various hypernuclei. To date, the lifetimes of only ${}_\Lambda H^3$, ${}_\Lambda H^4$, and of a mixture of ${}_\Lambda He^4$ and ${}_\Lambda He^5$ have been estimated The relative proportions of the various decay modes of given hypernuclei have provided some confirmation of a law which seems to govern the decay of strange particles in general. The weak forces between a Λ-hyperon and a nucleon which give rise to the non-mesonic decays are on the other hand still not clearly understood. The decay of several hypernuclei is dominated by the effects of a strong interaction among the final nuclear products. In this connection, the study of hypernuclei may even be a useful tool to study ordinary nuclear excited states.

Finally, hypernuclei with two bound Λ-hyperons have already been discovered [6]. Only one example of such a compound has provided information about the Λ-Λ interaction, but this information is unattainable in any other way. There was, until recently, no known particle that could produce more than two Λ-hyperons simultaneously, but the newly discovered Ω^--particle [7] could give three; it is therefore not inconceivable that hypernuclei with three Λ-hyperons may be found, as a result of the interaction of this particle with ordinary nuclei. The exclusion principle will then operate to determine the allowed energy levels that the various Λ-hyperons can occupy.

Bibliography

General articles on hypernuclei

Dalitz, R. H. *Proc. Rutherford Jub. Int. Conf.*, p. 103. Heywood & Co. Ltd, London. 1962.

Idem. 'The Nuclear Interactions of the Hyperons'. Lectures at the Summer School in Theoretical Physics, Bangalore. 1961. EFINS 62-9.

Telegdi, V. L. *Sci. Amer.*, 206, 50, 1962.

Burhop, E. H. S., Davis, D. H., and Zakrzewski, J. *Prog. nucl. Phys.*, 9, 155, 1964.

References

[1] Danysz, M. and Pniewski, J. *Phil. Mag.*, 44, 348, 1953.

[2] Bonetti, A., Levi Setti, R., Panetti, M., Scarsi, L., and Tomasini, G. *Nuovo Cim.* 11, 210, 330, 1954.

[3] Ammar, R. G., Choy, L., Dunn, W., Holland, M., Roberts, J. H., Shipley, E. N., Crayton, N., Davis, D. H., Levi Setti, R., Raymund, M., Skjeggestad, O., and Tomasini, G. *Nuovo Cim.*, 27, 1078,1963.

[4] Levi Setti, R. *Proc. Int. Conf. Hyperfragments*, S. Cergue, p. 17. March 1963, CERN Report 64-1.
Dalitz, R. H. and Levi Setti, R. *Nuovo Cim.*, 30, 489, 1963.

[5] Davis, D. H., Levi Setti, R., Raymund, M., Skjeggestad, O., Tomasini, G., Lemonne, J., Renard, P., and Sacton, J. *Phys. Rev. Lett.*, 9, 464, 1962.

[6] Danysz, M. *et al. Ibid.*, 11, 29, 1963.

[7] Fowler, W. B. and Samios, N. P. *Sci. Amer.*, 211, 36, 1964.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Polyacetylenic compounds in nature

A. W. Johnson

Plants of certain families, particularly Basidiomycetes and Compositae, contain a large number of compounds with conjugated acetylenic bonds. Several hundreds are now known. This article discusses the properties of these compounds and gives an account of their main structural patterns.

In 1948, a review [1] of acetylenic acids and derivatives could list only three or four naturally occurring compounds; today, several hundreds are known. This rapid increase has been largely due to the recognition of the very characteristic pattern of light absorption shown by the compounds; this pattern was discovered during early synthetic work on polyacetylenes. Infra-red and nuclear magnetic resonance spectra have been used in more recent structural studies. Accounts of the syntheses of polyacetylenes were published in 1960 [2] and 1961 [3], and there have been other reviews published since then [4, 5]; the naturally occurring compounds have been studied mainly in the laboratories of Sir Ewart Jones, of N. A. Sørensen, and of F. Bohlmann. The compounds fall into a number of distinct groups, and as the chemical relations are usually fairly obvious, these variations can be used to solve taxonomic problems [6]. This article will discuss the properties and syntheses of polyacetylenes, as well as their occurrence in nature.

Chemical properties

One of the outstanding chemical reactions of the polyacetylenes is hydrogenation. It is sometimes difficult to follow this, because of fission reactions, such as those of allylic or propargylic hydroxyl groups.

As a class, the compounds are often unstable in the crystalline state, especially in light, and the decomposition is accompanied by the development of colour. There are compounds known with half-lives of minutes and even seconds. Fortunately they are more stable in dilute solution, especially in the absence of light and oxygen; even so, they require delicate handling. The extent of our present knowledge is a tribute to the experimental skill of the workers in the field. Compounds containing terminal ethynyl groups (HC≡C—) are particularly unstable, and this contrasts with the relative stability of polyacetylenes containing bulky terminal groups. Thus ditert-butyldecayne, $Me_3C(C{\equiv}C)_{10}CMe_3$, forms orange needles that decompose at about 100°C.

The natural polyacetylenes are usually isolated by solvent extraction and purified by chromatography or counter-current extraction. Thin-layer chromatography is especially useful for confirming the identity or purity of these compounds.

Synthesis

There are now a number of good methods for coupling ethynyl compounds. The earliest of these used atmospheric oxygen as an oxidizing agent, in the presence of a cuprous salt:

$$2HC{\equiv}CR \xrightarrow{O_2[Cu^+]} RC{\equiv}C{-}C{\equiv}CR$$

This method is still in use, although some practical improvements have been introduced.

An important extension of this reaction is the coupling of an ethynyl compound with a bromo-ethynyl derivative in the presence of an amine, to form an unsymmetrical diacetylene:

$$RC{\equiv}CH + BrC{\equiv}CR' \xrightarrow{EtNH_2[Cu^+]} RC{\equiv}C{-}C{\equiv}CR'$$

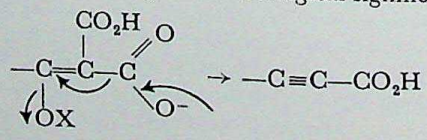
Another useful synthetic method is the dehydrohalogenation of acetylenic halides. This is exemplified by the following sequence:

$$2MeCHO + HC{\equiv}C{-}C{\equiv}CH \rightarrow$$
$$(MeCHOH{-}C{\equiv}C{-})_2 \rightarrow$$
$$(MeCHCl{-}C{\equiv}C{-})_2 \xrightarrow{NaNH_2} Me(C{\equiv}C)_3Me$$

It has been established, largely through the work of J. D. Bu'Lock and his collaborators [5], that the acetylenic chains of the fungal metabolites are built up from the same precursors as are required for the synthesis of saturated fatty acids (figure 1).

Thus the main unit for chain extension is malonyl-coenzyme A (figure 1a), which is added by repeated condensation to an initial acetyl-coenzyme A unit (figure 1b). This leads, by successive addition of C_2 units and elimination of carbon dioxide, to chains containing even numbers of carbon atoms. If compounds containing an odd number of carbon atoms in the chain are present, they have been formed by loss of carbon—by oxidation and decarboxylation—from the original metabolite. These facts were established by the use of intermediates containing carbon-14; the fate of individual atoms was followed by degradative studies.

However, the biological mechanism by which acetylenic bonds are formed in nature has not been established with any certainty. It is possible, for example, that the reaction is a progressive dehydrogenation of a carbon-carbon bond ($CH_2{-}CH_2 \rightarrow CH{=}CH \rightarrow C{\equiv}C$), but it has also been suggested that the facile eliminations observed with the enol esters (including phosphates) of acylmalonic acids might have biological significance:



$\rightarrow -C{\equiv}C{-}CO_2H$

Polyacetylenes from fungi

The simplest polyacetylenic compounds are those derived from fungi and micro-organisms. Most of the group belong to the C_9 or C_{10} series, with a small number of C_8 compounds and a few other structures larger than C_{10}. In general, the structural variations are less profound than those observed with the polyacetylenes of the higher plants, although the biochemical rearrangement of acetylenic bonds to allenes has so far been recognised

A. W. Johnson, *M.A., Sc.D., F.R.S.*

Was born in South Shields in 1917 and educated at Morpeth Grammar School, Northumberland, and Imperial College. After a period at I.C.I. Dyestuffs Division, he transferred to the University of Cambridge as Assistant Director of Research and then University Lecturer. Since 1955, he has been Sir Jesse Boot Professor of Organic Chemistry at the University of Nottingham.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

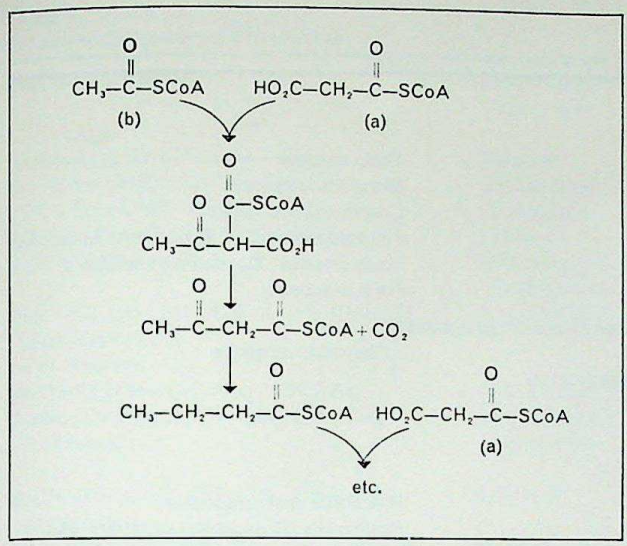


Figure 1 Biosynthesis of saturated fatty acids.

only in the fungal metabolites. One of the earliest of these substances to be studied was the antibiotic mycomycin(I), and in many ways this remains one of the most structurally remarkable of the naturally occurring polyacetylenes. It incorporates every known type of carbon-carbon unsaturation, and it was the first optically active allene to be isolated from a natural source. It proved to be very unstable and the later stages of the purification were carried out at −40°C in specially constructed apparatus. Mycomycin readily undergoes rearrangement with alkali to the more stable isomycomycin (II) with loss of the allenic function. This work dates from 1952; since then, both an isomer and the rearrangement product of mycomycin have been synthesized.

$$HC{\equiv}C{-}C{\equiv}C{-}CH{=}C{=}CH(CH{=}CH)_2{-}CH_2CO_2H$$

I

$$Me(C{\equiv}C)_3(CH{=}CH)_2CH_2{-}CO_2H$$

II

Another interesting point about mycomycin is that the organism that forms it was claimed to be *Nocardia acidophilus*, an Actinomycete species. However, it has been suggested that this observation may have been in error; it would be the only case in which a polyacetylene has been isolated from this group. As Basidiomycetes are known to produce mycomycin it is possible that the original culture may have been contaminated. The principal polyacetylenic allenes isolated from micro-organisms are listed in table I.

In two of the examples quoted in table I, the allene was accompanied by the corresponding acetylene, containing the group $-C{\equiv}C-CH_2-$ in place of $-CH{=}C{=}CH-$. This suggests that the pairs are interrelated biochemically, as they are chemically, by the movement of a proton. The structures of the polyacetylenic allenes form an interesting series and illustrate the ability of the fungi progressively to shorten the fatty acid chain, and to effect a variety of oxidations of functional groups. This relationship is even more apparent in the main C_9 and C_{10} groups of non-allenic fungal metabolites. These were first detected by means of their characteristic absorption spectra in various species of Basidiomycetes. The initial observations were made in New York by M. Anchel, and the subsequent detailed studies were by Sir Ewart Jones [2]. Tables II and III list most of the known C_9 and C_{10} fungal polyacetylenes isolated by these workers.

Table I
Polyacetylenic allenes from micro-organisms

A. $HC{\equiv}C{-}C{\equiv}C{-}CH{=}C{=}CH{-}R$	
R= CH_2OH	*Cortinellus barkleyanus; Marasmius* spp.
$CH_2{-}CH_2OH$ (−) (marasin)	
$CH_2{-}CH_2OH$ (+)	*Aleurodiscus roseus*
$CH_2{-}CO_2H$ (Me)	
$CH_2{-}CH_2{-}CH_2OH$	*Odontia bicolor*
$CHOH{-}CH_2{-}CH_2OH$	
$CHOH{-}CH_2{-}CH_2{-}CO_2H$ (nemotinic acid)	*Poria* spp.
$CH{-}CH_2{-}CH_2$ (nemotin)	
$O{-}CO$	
$CH{=}^{c}CH{-}CH{=}^{t}CH{-}CH_2{-}CO_2H$ (mycomycin)	*Nocardia* sp. (?)
$CH_2{-}CHOH(CH_2)_3CO_2Me$	*Odontia bicolor*
B. $H_2C{=}C{=}CH(C{\equiv}C)_2R$	
R= $CH{=}^{c}CH.CH_2.CO_2H$ (drosophilin D)	*Psathyrella (Drosophila) subatrata*
C. $Me(C{\equiv}C)_2CH{=}C{=}CH{-}R$	
R= $CH(OH){-}CH_2{-}CH_2{-}CO_2H$ (odyssinic acid)	*Poria* spp.
$CH{-}CH_2{-}CH_2$ (odyssin)	
$O{-}CO$	

Table II
C_9 polyacetylenes from micro-organisms

A. $H(C{\equiv}C)_3R$	
R= $CH{=}CH{-}CO_2H$	*Poria sinuosa; Psilocybe sarcocephela*
$CH{=}CH{-}CO{-}NH{-}CH(CO_2H)CHMe_2$	*Poria sinuosa*
$CH{=}CH{-}CHO$	*Coprinus quadrifidus; Polyporus biformis*
$CH{=}CH{-}CH_2OH$	
$CH{-}CH{-}CH_2OH$ (biformyne I)	
O	
$CHOH{-}CHOH{-}CH_2OH$ (2 isomers)	
B. $H(C{\equiv}C)_2CH{=}^{c}CHR$	
R= $CH_2{-}CH_2{-}CO_2H$	*Psathyrella (Drosophila) subatrata*
$CH_2{-}CH_2{-}CH_2OH$	*Aleurodiscus roseus*
$CHOH{-}CHOH{-}CH_2OH$ (2 isomers)	*Coprinus quadrifidus*
C. $R(C{\equiv}C)_2R'$	
R= $HO{-}CH_2{-}CH_2$, $HO_2C{-}CH_2$ R′= $CH{=}CH{-}CH_2OH$	*Polyporus sinuosa*
$CH{=}CH{-}CH_3$	*Cortinellus berkleyanus*
$HO{-}CH_2{-}CH_2$ / $CHOH{-}CH_2{-}CH_3$	*Clitocybe rhizophera*
$HO{-}CH_2{-}CH_2$ / $CO{-}CH_2{-}CH_3$	

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Table III

C_{10} polyacetylenes from micro-organisms

A.		
$R(C{\equiv}C)_2R'$		
R= CO_2H	R′=CH=CH—CO_2H	*Poria sinuosa*
	CH_2—CH_2—CO_2H	*Merulius lacrymans*
CHO	CH=CH—CO_2H	*Coprinus quadrifidus*
CH_2OH	CH=CH—CO_2H	*Pleurotus ulmarius; Tricholoma panaeolum*
	CH=CH—CH_2OH	*Poria sinuosa; Coprinus quadrifidus*
	CH_2—CHOH—CO_2H	*Poria sinuosa*
Me	$CH^{t}{=}CH$—CO_2H(Me) (*trans*-dehydromatricaria ester)	*Pleurotus ulmarius*
	CH=CH—CHO	*Pleurotus ulmarius*
	CH=CH—CH_2OH (dehydromatricariol)	*Pleurotus ulmarius*
B.		
$R(C{\equiv}C)_2R'$		
R= (Me)HO_2C—CH=CH	R′= CH=CH—CO_2H(Me)	*Polyporus anthracophilus; Psathyrella (Drosophila) subatrata*, etc.
$HOCH_2$—CH=CH	CH=CH—CO_2H(Me)	*Polyporus anthracophilus*, etc.
MeCH=CH	CH=CH—CO_2H(Me) (matricaria esters)	*Polyporus anthracophilus*, etc.
	CH=CH—CH_2OH (matricariol)	*Polyporus anthracophilus*, etc.
HO_2C—CH_2—CH_2	CH=CH—CO_2H	*Polyporus anthracophilus; Merulius lacrymans*
$HOCH_2$—CH_2—CH_2	CH=CH—CO_2H(Me)	*Polyporus anthracophilus*
	CH=CH—CH_2OH	'B244'
Me—CH_2—CH_2	CH=CH—CH_2OH	'B244'
Me	CH=CH—CH_2—CHOH—CO_2H	*Poria sinuosa*

An examination of these structures suggests that all might be derived from n-decanoic acid, $Me(CH_2)_8CO_2H$, by plausible biochemical reactions. One important generalization is that most of the C_9 compounds contain a free ethynyl group, HC≡C—, while most of the C_{10} compounds contain a terminal methyl group (or an oxidized methyl group such as hydroxymethyl, formyl, or carboxylic acid). This suggests that the metabolites containing an odd number of carbon atoms are formed by loss of one carbon atom—by loss of carbon dioxide or possibly formaldehyde—from those containing an even number of carbon atoms. There are, however, many exceptions to this rule, such as those of table II, section C. Oxidations, including dehydrogenations, are clearly commonplace reactions in this series, especially the sequences Me → CH_2OH → CHO → CO_2H → CO_2 and CH=CH → CH—CH (O) → CHOH—CHOH. Moreover, a variety of functional derivatives of the carboxyl group, —$CONH_2$, —CONHR, and —CN for example, can occur as in the metabolites of *Poria sinuosa* and *Polyporus anthracophilus*.

Table IV

C_{10} polyacetylenes from Compositae

Me—CH_2—$CH_2(C{\equiv}C)_2CH^{c}{=}CH.CO_2Me$ (lachnophyllum ester)	Astereae
Trans isomer	Astereae
Me—CH_2—CHOH$(C{\equiv}C)_2CH$=CH—CO_2Me (as angelic ester)	Astereae
MeCH=CH$(C{\equiv}C)_2CH_2$—CH_2—CO_2Me	Astereae; Anthemideae
$MeCH^{c}{=}CH(C{\equiv}C)_2CH^{c}{=}CH$—$CO_2Me$ (*cis*-matricaria ester)	Astereae; Anthemideae; Cynareae
di-*trans* isomer (*trans*-matricaria ester)	Astereae; Anthemideae; Cynareae
MeCH=CH—C≡C—CH= (CO, O) (matricaria lactone)	Anthemideae
$MeCH^{t}{=}CH(C{\equiv}C)_2CH^{t}{=}CH$—$CH_2OAc$ 2-*trans*-8-*cis* isomer	Astereae
$Me(C{\equiv}C)_2CH^{c}{=}CH$—$CO_2Me$ (*cis*-dehydromatricaria ester)	Astereae; Anthemideae
Trans isomer	Astereae; Anthemideae
$Me(C{\equiv}C)_3CH$=CH—CO.NH—CH_2—$CHMe_2$	Anthemideae
MeC(SMe)=CH$(C{\equiv}C)_2CH$=CH—CO_2Me and isomers	Anthemideae

Polyacetylenes from the higher plants

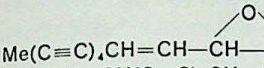
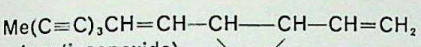
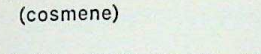
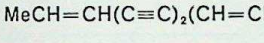
A much larger group of polyacetylenes occurs in the higher plants, particularly those of the Compositae, and to a much lesser extent those of the Umbelliferae and the Araliaceae. The taxonomic aspects of the polyacetylene-containing plants have been discussed in detail in the reviews by Bohlmann [4] and particularly in that by Sørensen [6], who have themselves done nearly all the work in this field. The largest groups of polyacetylenic compounds from Compositae are either C_{10} or C_{13} compounds; most of the Umbelliferae and Araliaceae polyacetylenes are C_{17} compounds. Allenes have not been detected among the metabolites of the higher plants, but several other variations of the unsaturated chain, particularly the formation of benzenoid and heterocyclic rings, are commonplace.

The Compositae are usually subdivided into the Liguliflorae (Cichorieae), which do not contain polyacetylenes, and the Tubuliflorae, which do. These latter

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

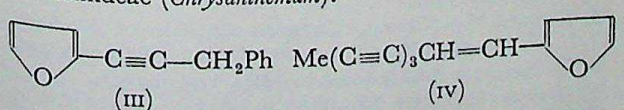
Table V
C_{13} polyacetylenes from Compositae

$Me(C{\equiv}C)_5CH{=}CH_2$	Heliantheae; Cynareae
	Cynareae
$Me{-}CH{=}CH(C{\equiv}C)_4CH{=}CH_2$	Heliantheae; Cynareae; Inuleae
$HOC{-}CH{=}CH(C{\equiv}C)_4CH{=}CH_2$	Heliantheae; Cynareae; Inuleae
$HOCH_2{-}CH{=}CH(C{\equiv}C)_4CH{=}CH_2$	Heliantheae; Cynareae; Inuleae
$Me(C{\equiv}C)_3(CH{=}CH)_3H$	Heliantheae; Anthemideae
 (ponticaepoxide) and isomers	Anthemideae
$Me(C{\equiv}C)_3(CH{=}CH)_2CH_2{-}CH_2OAc$	Anthemideae
$MeCH{=}CH(C{\equiv}C)_3CH{=}CH{-}CH{=}CH_2$ (cosmene)	Anthemideae; Heliantheae
 and isomers	Cynareae
$HOC{-}CH{=}CH(C{\equiv}C)_3CH{=}CH{-}CH{=}CH_2$	Anthemideae
$HO{-}CH_2{-}CH{=}CH(C{\equiv}C)_3CH{=}CH{-}CH{=}CH_2$	Anthemideae
$Me(C{\equiv}C)_2(CH{=}CH)_3CH_2{-}CH_2OAc$	Anthemideae
$MeCH{=}CH(C{\equiv}C)_2(CH{=}CH)_3H$	Heliantheae
	Heliantheae
$AcO.CH_2.CH{=}CH(C{\equiv}C)_2(CH{=}CH)_3H$	Heliantheae
$MeCH{=}CH(C{\equiv}C)_2(CH{=}CH)_2CHOH{-}CH_2OH$	Cynareae

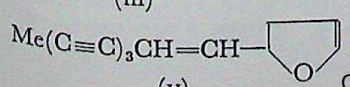
are further subdivided into twelve tribes. Of these the Astereae, Inuleae, Heliantheae, Helenieae, Anthemideae, and Cynareae are the most important from the point of view of polyacetylenic content. The main acyclic polyacetylenes of the C_{10} and C_{13} groups from Compositae are listed in tables IV and V.

These tables are by no means exhaustive, but they illustrate the common variations of polyacetylenic structures in the metabolites of Compositae. It is apparent, for example, that the shorter chains are favoured in Astereae; that a triple bond is frequently adjacent to the terminal methyl group in the products from Anthemideae, but in Heliantheae and Cynareae the triple bond is usually replaced by a double bond—a terminal propenyl group; and that there is the greatest tendency towards oxidation of double bonds to epoxides and glycols (and sometimes chlorohydrins) in Cynareae. More detailed considerations of the bearing of these chemical features on the taxonomic problems of the Compositae are given in Sørensen's review [6].

The polyacetylenic group is reactive chemically and lends itself to several further chemical variations. Reduction of a single acetylenic bond and subsequent oxidation can give an epoxide. If the oxidation involves a chain extending over four carbon atoms, a furan or dihydrofuran may result, and several acetylenic furans have in fact been isolated. Possibly the best known is carlina oxide (III) but structures (IV) and (V) are further examples which have been isolated from Cynareae as well as Anthemideae (*Chrysanthemum*).

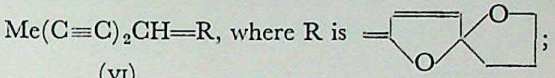


(III) (IV)

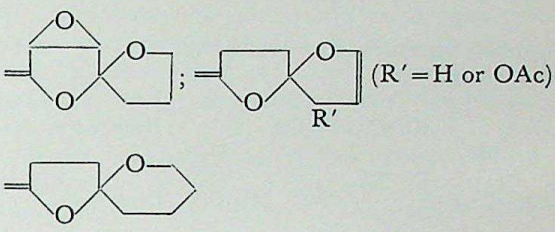


(V)

A further elaboration, so far characteristic of Anthemideae, is the spiroketal system, as in compound VI, which is found in metabolites of certain *Chrysanthemum* spp. The structures of the individual compounds have been determined by Bohlmann and his collaborators as



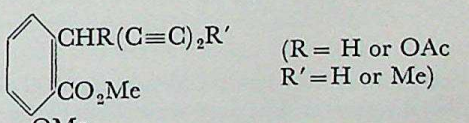
(VI)



In many cases, one plant may furnish more than a dozen polyacetylenic compounds, and some of the compounds are clearly intermediate in the formation of others. Plausible mechanisms for the formation of these spirans from unsaturated chains have been suggested.

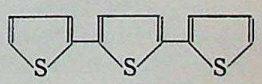
Polyacetylenes containing phenyl groups. Another common variation is the presence of a phenyl ring formed by the cyclization of an unsaturated C_6 chain, although the precise mechanism by which the reaction occurs is not yet established. Phenyl-substituted polyacetylenes have been reported from Heliantheae and Cynareae, as well as from Anthemideae. Some examples are included in table VI.

A further group, so far restricted to Anthemideae, comprises derivatives of salicylic acid. The derivatives (VII), which include frutescin, have been isolated from *Chrysanthemum foeniculaceum* and it seems probable that a different type of cyclization of the unsaturated chain is involved in this series:



(R = H or OAc
R′ = H or Me)

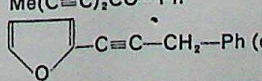
(VII)



(VIII)

Polyacetylenes containing thiophene rings. It is possible to convert a diacetylene into a thiophene in the laboratory, and many examples have been provided by Bohlmann and by K. E. Schulte. The possibility of a similar bio-

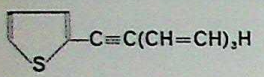
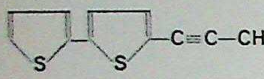
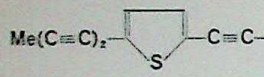
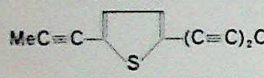
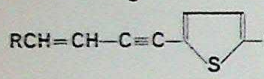
Table VI
Polyacetylenes containing phenyl rings from Compositae

$Me(C{\equiv}C)_3Ph$	Heliantheae
$MeCH{=}CH(C{\equiv}C)_2Ph$	Heliantheae
$H(C{\equiv}C)_2CH_2Ph$	Anthemideae
$Me(C{\equiv}C)_2CH_2Ph$ (capillene; agropyrene)	Anthemideae
$Me(C{\equiv}C)_2CHOAc{-}Ph$	Anthemideae
$Me(C{\equiv}C)_2CO{-}Ph$	Anthemideae
	Cynareae

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Table VII
Some acetylenes containing thiophene rings from Compositae

	Anthemideae
	Anthemideae; Cynareae
	Cynareae
(with numerous variations of terminal methyl and vinyl groups)	
	Heliantheae
	Cynareae
(R=Me, CH_2OH, CH_2OAc, CHO)	

The main representatives of this group are listed in table VIII.

Finally, there is a distinct group of acetylenic acids which occur in a few species of Olacaceae and Santalaceae. They occur in various parts of these trees or bushes, but particularly in the seed fat. These compounds were the first naturally occurring acetylenic compounds to be recognized, although most of them contain only one triple bond. Examples are tariric acid, first isolated in 1892, $Me(CH_2)_{10}C{\equiv}C(CH_2)_4CO_2H$, and ximenynic acid, $Me(CH_2)_5CH{=}CH{-}C{\equiv}C(CH_2)_7CO_2H$.

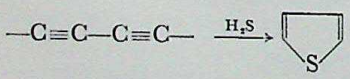
Besides these, there are also a few polyacetylenic fatty acids, of which the following are the best known; it is probable that the Olacaceae also contain hydroxy-polyacetylenic acids.

$CH_2{=}CH(CH_2)_4(C{\equiv}C)_2(CH_2)_7CO_2H$ (isanic acid)	Olacaceae
$CH_2{=}CH(CH_2)_2CH{=}CH(C{\equiv}C)_2(CH_2)_7CO_2H$ (bolekic acid)	Olacaceae
$C_4H_9CH{=}CH(C{\equiv}C)_2(CH_2)_7CO_2H$	Santalaceae

Table VIII
Polyacetylenes from Umbelliferae and Araliaceae

$C_6H_{13}(CH{=}CH)_2(C{\equiv}C)_2CH{=}CH{-}CH_2OH$ (oenanthol)	Umbelliferae
$C_6H_8(CH{=}CH)_3(C{\equiv}C)_2CH_2{-}CH_2{-}CH_2OH$(cicutol)	Umbelliferae
$C_3H_7{-}CHOH(CH_2)_2(CH{=}CH)_2(C{\equiv}C)_2CH{=}CH{-}CH_2OH$ (oenanthatoxin)	Umbelliferae
$C_3H_7{-}CO(CH_2)_2(CH{=}CH)_2(C{\equiv}C)_2CH{=}CH{-}CH_3$	Umbelliferae
$C_3H_7{-}CHOH(CH{=}CH)_3(C{\equiv}C)_2CH_2{-}CH_2{-}CH_2OH$ (cicutoxin)	Umbelliferae
$C_7H_{15}CH{=}CH{-}R{-}(C{\equiv}C)_2CO{-}CH{=}CH_2$ R= CH_2 (falcarinone), CHOH, or CO	Umbelliferae; Araliaceae

chemical reaction was recognized by F. Challenger as early as 1953. Certainly the incorporation of sulphur into polyacetylenic compounds is well recognized, particularly the addition of hydrogen sulphide to a diacetylene to form a thiophene ring:



This ring is common in the Anthemideae, especially *Tagetes* and *Tripleurospermum*, but acetylenic thiophenes also occur in Heliantheae and Cynareae. The great majority of these thiophenes are C_{12} and C_{13} compounds (table VII). Cysteine or methionine, as well as hydrogen sulphide, can act as the source of sulphur, and it is likely that the naturally occurring terthienyl (VIII) arises by similar additions to a polyacetylenic system. Other ring systems containing more than one sulphur atom in the ring have been described by Sørensen.

Larger polyacetylenes from the higher plants. A small group of C_{14} polyacetylenes has been isolated from Compositae. They include two isobutylamides, anacyclin (IX; R = Me—CH_2—CH_2—) and dehydroanacyclin (IX; R = Me—CH=CH—), the insecticidal principles of *Anacyclus pyrethrum* de Candolle [7]:

$$R(C{\equiv}C)_2(CH_2)_2(CH{=}CH)_2CO{-}NH{-}CH_2{-}CHMe_2$$
(IX)

A group of C_{17} polyacetylenes occurs in plant families other than Compositae, particularly Umbelliferae. Among these C_{17} compounds are the highly toxic principles of *Oenanthe crocata* L. and *Cicuta virosa* L. [8].

It should be stressed that the acetylenic content of plants varies during the growing season and varies in different parts of the plant, and that these are aspects of the general problem that only few authors have considered so far. Whether the extraordinary rate of discovery of new acetylenes from natural sources will be maintained can only be surmised, but there is no sign of abatement at present, and there are still very many genera, and even families, of plants which have scarcely been examined for their polyacetylenic content. Moreover, the use of ultraviolet spectra to detect the polyacetylenes may well have caused some of the modified chromophores to be overlooked, and it is clear that many of these metabolites remain to be discovered.

References

[1] Johnson, A. W. 'The Chemistry of the Acetylenic Compounds'. Vol. II. 'The Acetylenic Acids'. E. Arnold & Co., London. 1948.
[2] Jones, E. R. H. *Proc. chem. Soc.*, 199, 1960.
[3] Sørensen, N. A. *Ibid.*, 98, 1961.
[4] Bohlmann, F., Bornowski, H., and Arndt, C. *Fortschr. chem. Forsch.*, 4, 138, 1962.
[5] Bu'Lock, J. D. 'Polyacetylenes and Related Compounds in Nature', in 'Progress in Organic Chemistry' (Sir James Cook and W. Carruthers, Editors), p. 86. Butterworths, London. 1964.
[6] Sørensen, N. A. 'Chemical Taxonomy of Acetylenic Compounds' in 'Chemical Plant Taxonomy' (T. Swain, Editor), p. 219. Academic Press, London and New York. 1963.
[7] Crombie, L. *J. chem. Soc.*, 999, 1955.
[8] Anet, E. F. L., Lythgoe, B., Mirrish, S., and Trippett, S. *Ibid.*, 309, 1953.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Coccoliths

Digitized by Arya Samaj Foundation Chennai and eGangotri

Maurice Black

Very fine particles of chalk contain tiny rosettes of calcite crystals that were long thought to be inorganic in origin. They are now known to be the relics of unicellular algae called coccospheres. This article describes the life cycles of the algae, which are often abundant and important in marine ecology, and the structures of the fossils—coccoliths—which are valuable to geologists for dating.

If very fine particles of ordinary chalk, such as are used in the manufacture of whiting, are examined under an electron microscope, they are seen to contain innumerable little rosettes of calcite crystals about 1 μ across and quite different from the rough fragments obtained by crushing harder limestones. Figures 1 and 2 are electron micrographs of the crystals. They were first noticed as long ago as 1836 by C. G. Ehrenberg, using an ordinary microscope, who remarked on their extraordinary abundance in samples of chalk which he got from the island of Rügen in the Baltic; he regarded them as inorganic concretions, similar to the spherulites formed by radial growth of crystals about a nucleus. They came to be known as 'morpholiths' or 'crystalloids', and their inorganic origin was generally accepted until 1861, when H. C. Sorby of Sheffield published the results of his researches on the English chalk [1]. Sorby found great quantities of crystalloids, as Ehrenberg had done, but went on to observe that they differed in several respects from inorganic spherulites. For instance, he found that each crystalloid was shaped like an oval watch-glass, with a curvature suggesting that it originally formed part of the shell around a sphere (figure 1). Indeed, he succeeded in finding such spheres entirely clothed by crystalloids (figure 3). From these observations, he concluded that the chalk crystalloids were more likely to have been formed organically, as part of the external skeleton of a living organism, than purely inorganically.

At about the same time, the first samples of deep-sea ooze were raised from the floor of the Atlantic Ocean and examined by T. H. Huxley and G. C. Wallich. These samples contained innumerable round and oval bodies, much like the chalk crystalloids; Huxley at first doubted their organic nature, but because their general shape reminded him of the cells of the green alga *Protococcus*, he called them coccoliths. Wallich found little hollow spheres built out of coccoliths. He called these coccospheres, and a few years later he was able to announce the discovery of living coccospheres swimming freely near the surface of the ocean.

These investigations of Huxley and Wallich formed part of a very careful investigation of the sea-bed between Ireland and Newfoundland to discover the properties of the floor upon which the first transatlantic telegraph cables were shortly to be laid. After this practical problem had been dealt with, the study of coccoliths continued as a piece of pure research, linked up with wider studies. One of these was of the nature of primitive life in the oceans; another was of the progressive locking up of vast amounts of calcium carbonate on the sea-floor, a process that had clearly been going on ever since the chalk was deposited some 100 million years ago.

About the beginning of the present century, the coccospheres acquired a practical importance. With the discovery that enormous concentrations of these primitive plants live near the surface of the ocean, their importance as primary producers in the food-chain leading through the zooplankton to the fishes became apparent, and a study of their migration and seasonal fluctuations is now accepted as an essential part of fisheries' research. In the last two or three years German and Austrian petroleum geologists have been making increasing use of these fossils for dating samples raised in the course of drilling [5, 6, 17]. Because of their minute size, enough coccoliths can be extracted from very small samples of well-cuttings to give an answer when other methods fail.

The living organism

The living coccospheres proved to be unicellular algae belonging to the Chrysophyceae: that is, they are very primitive plants related to the seaweeds. Since Wallich's day, improved methods of collecting have led to the discovery of a considerable number of species, nearly all of them living in the open ocean. They are too small to be collected in a plankton-net, and are usually obtained by centrifuging samples of water taken at measured distances below the surface. From these samples, individual plants can be picked out with a micropipette; they may then be kept alive in the laboratory and used to build up pure cultures. Such cultures are maintained at the Botany School at Cambridge, the Plymouth Laboratory, and the Institute for Marine Biology at Oslo; they provide a reserve of material for studying the physiology and life-history of individual species.

In samples collected from the open ocean, most of the coccospheres are free-swimming, and propel themselves through the water by means of a pair of flagella arising from one pole of the cell. Like other plants, they use the energy of sunlight to synthesize foodstuffs from carbon dioxide and water, and possess chromatophores for this purpose. It is because of their dependence on photosynthesis that they can flourish only in the upper layers of the ocean, within reach of sunlight. A few species have been observed to ingest solid food, but this method of nutrition is exceptional and always subordinate to photosynthesis.

The life-histories of several species have now been followed in detail, and the results have turned out to be quite unexpected. *Crystallolithus hyalinus* is an actively swimming species from the N-E Atlantic that, when kept in culture, reproduces itself by fission to produce

M. Black, *M.A.*
Was born in Scarborough, Yorkshire, in 1904 and educated at the University of Cambridge and Princeton University. He is now a Fellow of Trinity College and a Reader in Sedimentary Petrology in the University of Cambridge. His research interests were in shallow-water marine deposits in the West Indies; they are now in studies of English Chalk and of deep sea deposits.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

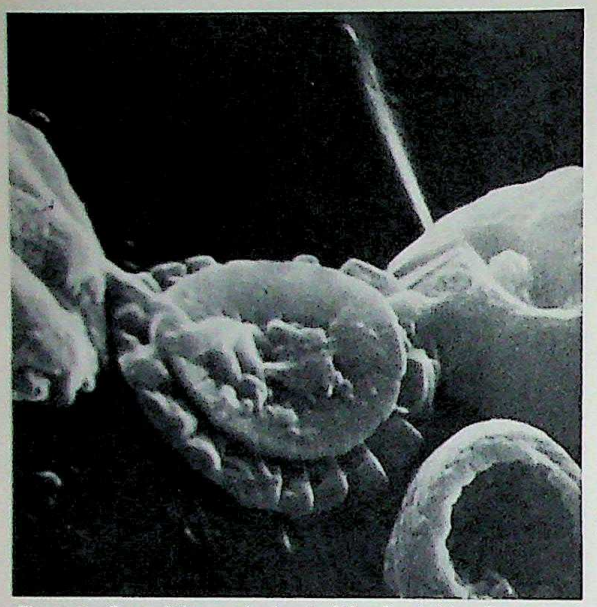


Figure 1 Coccoliths washed out of the Cambridge Greensand. The central specimen, an undescribed species of *Biscutum*, consists of two disks curved to fit the surface of the coccosphere. (×10 000)

daughter cells that are like their parents. However, after a few weeks these cease to swim about, and they settle down to the bottom of the flask as a dark olive-brown film [2]. The cells then grow in size, and ultimately change into a form previously regarded as a separate species, *Coccolithus pelagicus*, which bears coccoliths of an entirely different kind (figure 4). Observations of cultures at Plymouth over a 12-month period have shown that there is a regular alternation between the motile *Crystallolithus* phase and that of the non-motile *C. pelagicus* during the period.

In *Syracosphaera carterae* and several other species studied by Mary Parke [3], the motile coccolith-bearing stages that live in the open sea have been found to alternate with sessile phases looking like certain genera of Chrysophyceae that had been previously discovered inhabiting the sea-cliffs at Westgate and also at St Andrew's Bay in Scotland. Some of these are filamentous, others are colonial forms of various habits; and all of them are so different from typical coccospheres that they had been thought to belong to separate families.

The life-histories of the great majority of species remain unknown, but the few that have been worked out suggest that there may be a fundamental difference between the species that inhabit coastal waters and those that prefer to live in mid-ocean. In the coastal species, the free-swimming generations appear to alternate with filamentous or other sessile forms that colonize rocks or some other solid foundation; the oceanic species, living out of reach of the sea-floor or the shore, probably have cyst-like resting stages similar to *C. pelagicus*. This is non-motile, but it does not require a solid foundation to support it and can remain suspended in the upper layers of the ocean.

Structure and development of coccoliths

The resolving power of an ordinary biological or petrological microscope is not good enough to show up the finer structures of coccoliths. The wavelength of light near the middle of the visible spectrum is about one half-micron, and the component crystals of many coccoliths are much smaller than this. Useful information can be obtained by using polarized light, but although this method is often helpful in the routine identification of species, the results are not always easy to interpret in terms of actual structure. For this purpose the higher resolutions obtainable with an electron microscope are a great advantage. Calcite crystals, of which all known coccoliths are constructed, are opaque to the electron beam, and attempts to photograph the actual coccoliths by transmission give shadows with little or no surface detail. More useful pictures, such as figure 1, can be obtained by using a scanning microscope, or by photographing carbon replicas, which are transparent. These are prepared by evaporating, *in vacuo*, a thin film of carbon on to the coccoliths, and shading this with a heavy metal such as gold, platinum, or chromium. The original calcite can then be removed by hydrochloric

Figure 2 A characteristic Chalk coccolith, *Colvillea barnesae*, from Turonian Chalk near Newmarket. (No. 3091, ×10 000)

Figure 3 A fossil coccosphere from the Danian Chalk of Stevns Klint, Denmark. (No. 11 735, ×6000)

Figure 4 A damaged specimen of *Coccolithus pelagicus* from the Biscay Abyssal Plain, showing the double central pore surrounded by an inner zone of rhombohedral crystals, and an outer zone of overlapping rays. (No. 10 020, ×5000)

Figure 5 Rhombohedral calcite crystals in one of the oldest known European coccoliths, *Alvearium dorsetense*, from the Lower Lias of Dorset. (No. 13 023, ×8000)

Figure 6 *Coccolithus britannicus* from the Kimeridge Clay of Dorset. (No. 15 165, ×8000)

Figure 7 A circular species of *Coccolithus* from the Kimeridge Clay, illustrating the spiral arrangement of crystals present in most coccoliths. (No. 15 159, ×9300)

Figure 8 *Rhabdosphaera* from the Sutterby Marl (Aptian) of Lincolnshire. Coccoliths with this structure become increasingly common towards the top of the Lower Cretaceous. (No. 16 051, ×7000)

Figure 9 *Lithastrinus* from the Gault at Folkestone. A simply constructed coccolith in which the overlapping calcite crystals can be clearly seen. (No. 13 505, ×11 700)

Figure 10 One of the numerous species of *Rhabdosphaera* from the Gault. In the centre is the broken stump of a tubular stalk. (No. 13 479, ×7000)

Figure 11 *Stephanolithion*, a wheel-shaped coccolith which ranges from the Oxford Clay to the Lower Cretaceous. (No. 13 506, ×15 000)

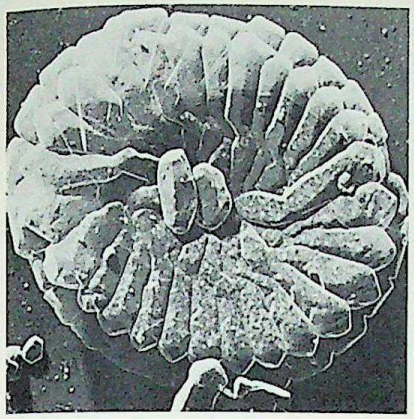
Figure 12 One of the commonest Lower Cretaceous species of *Coccolithus*, showing the two disks and central pore characteristic of this genus. (No. 10 386, ×8000)

Figure 13 *Cribrosphaera murrayi*, with a central sieve-plate. First discovered in Russia, it is now known to be common in the Cambridge Greensand. (No. 14 711, ×13 000)

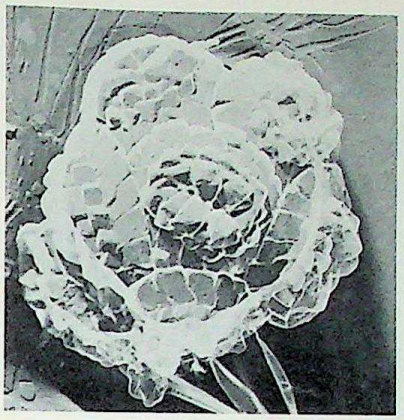
The specimens illustrated are identified by their serial numbers in the collection of electron micrographs at the Sedgwick Museum.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

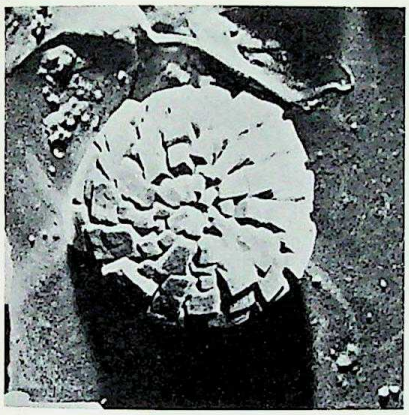


2

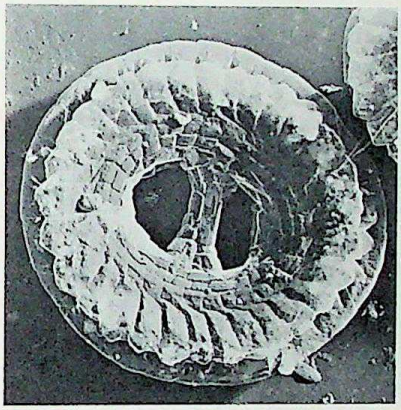


3

4

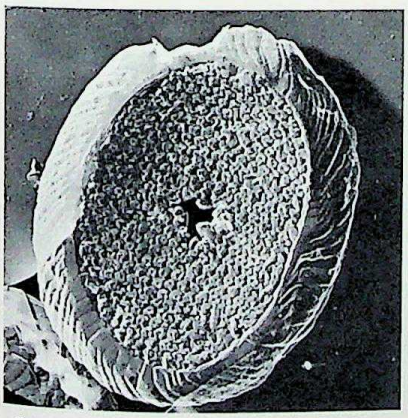


5

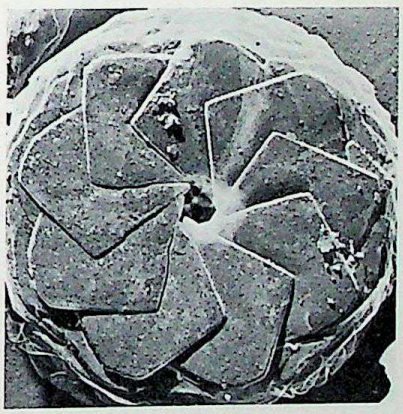


6

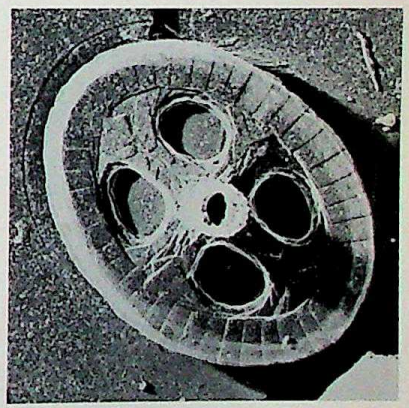
7



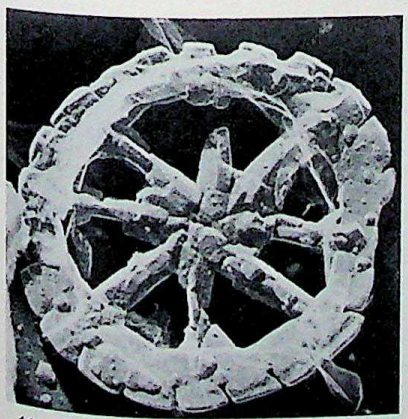
8



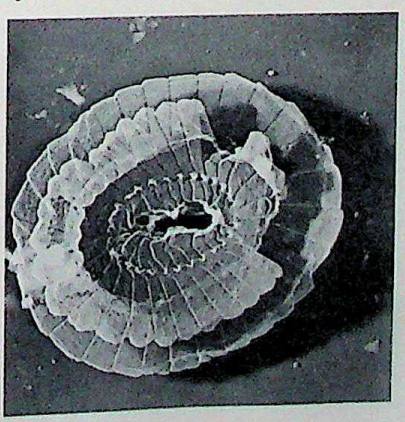
9



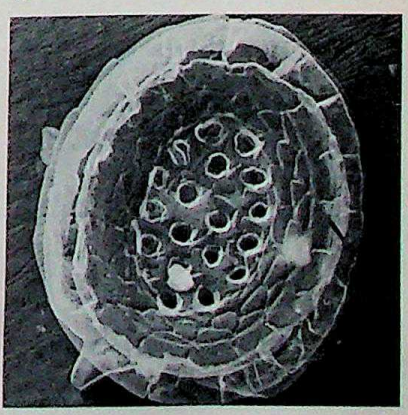
10



11



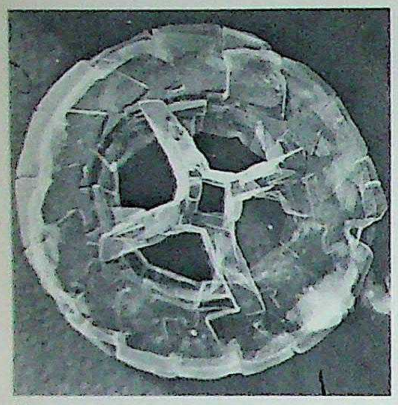
12



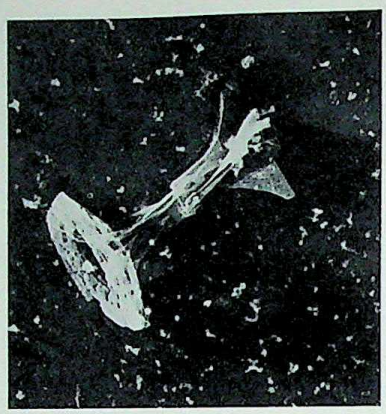
13

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

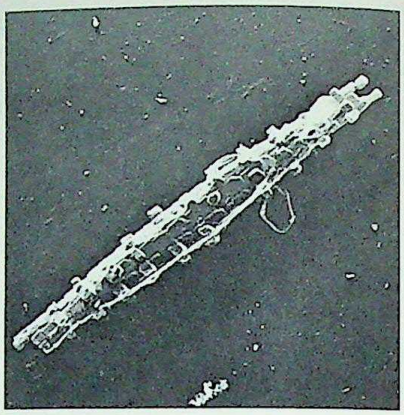
Digitized by Arya Samaj Foundation Chennai and eGangotri



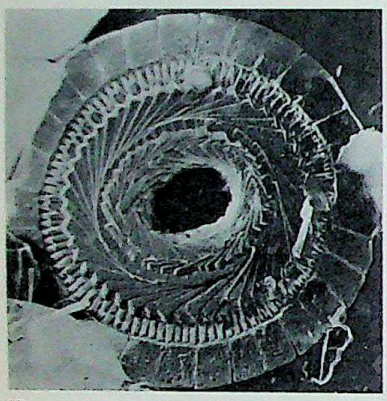
14



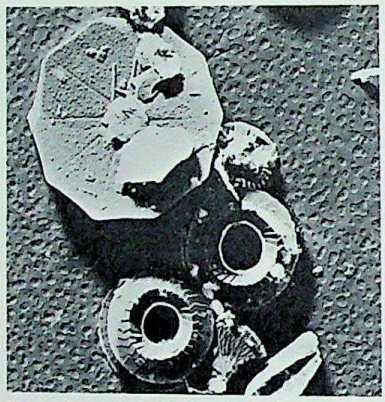
15



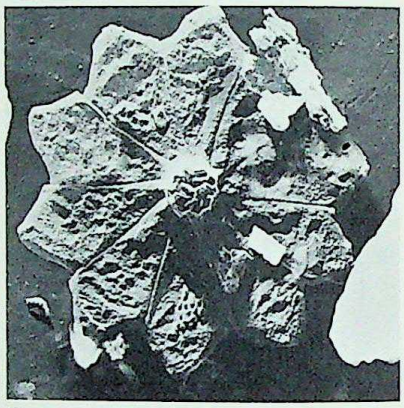
16



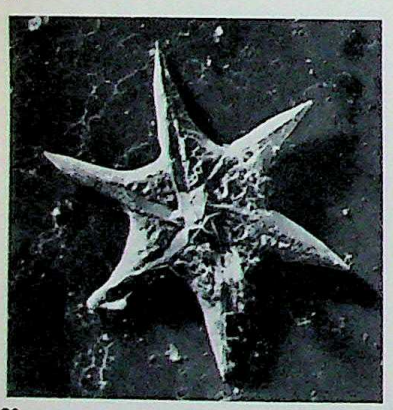
17



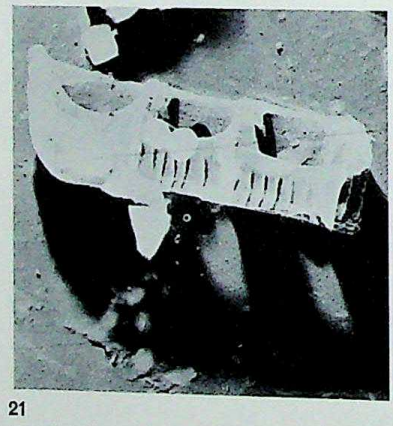
18



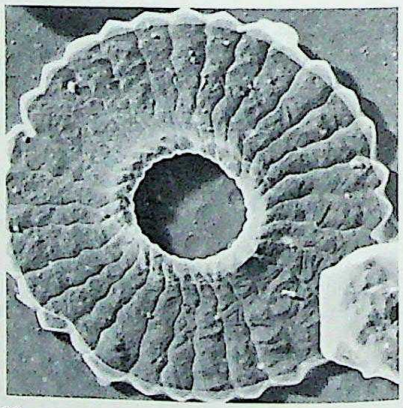
19



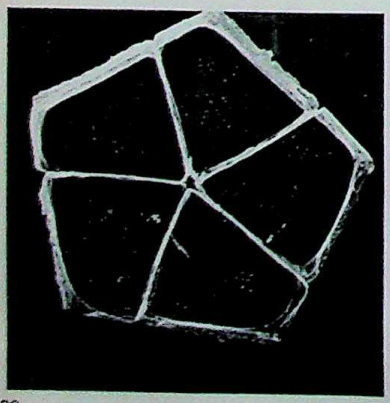
20



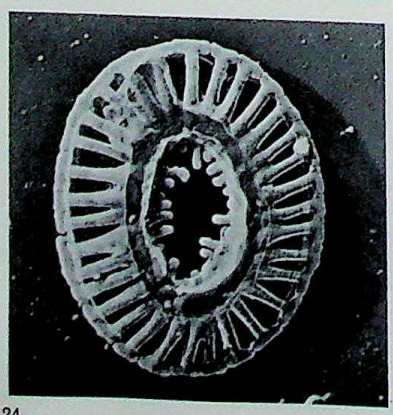
21



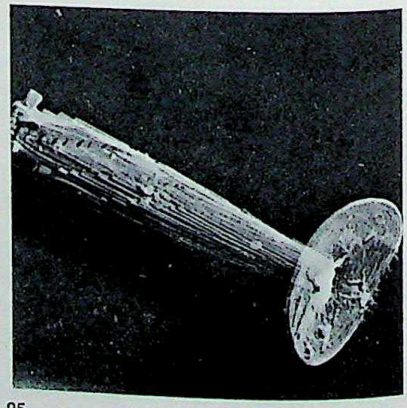
22



23



24



25

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Figure 14 *Deflandrius* from the Cambridge Greensand, showing the central cross and 16 modified rhombohedra in the outer rim. The stem is broken, revealing a four-sided central canal. (No. 14 725, ×10 000)

Figure 15 A complete specimen of *Deflandrius* with fin-like expansions at the end of the stem. (No. 13 490, ×5300)

Figure 16 *Microrhabdulus belgicus*, which is probably the stalk of a *Rhabdosphaera* (cf. figure 25), is decorated with minute calcite rhombs. (No. 3832, ×6000)

Figure 17 *Blackites spinosus*, from the Lower Tertiary of Denmark. This is one of the most elaborately constructed coccoliths yet discovered, in spite of its small size (0·005 mm). (No. 11 939, ×10 500)

Figure 18 *Discoaster perplexus* (10-sided) and *Umbilicosphaera mirabilis* (circular), showing the difference between the structural patterns of discoasters and coccoliths. (No. 11 253, ×4000)

Figure 19 *Discoaster barbadiensis*, first discovered in the Lower Tertiary rocks of Barbados, and later found in rocks of the same age in many distant parts of the world. (No. 11 949, ×6000)

Figure 20 *Discoaster lodoensis*, a six-rayed species with world-wide distribution in the Lower Tertiary. (No. 15 771, ×2500)

Figure 21 *Isthmolithus recurvus*, a peculiar boat-shaped coccolith which existed for a short time during the Lower Tertiary; it serves as a useful zone-fossil. (No. 11 953, ×6000)

Figure 22 *Calcidiscus*, a simply constructed coccolith with one disk only. This specimen is from the Upper Tertiary (Pliocene) of Indonesia. (No. 15 356, ×15 000)

Figure 23 A single plate of *Braarudosphaera bigelowi*, consisting of five peculiarly shaped calcite crystals. (No. 15 750, ×6000)

Figure 24 *Coccolithus huxleyi*, the most widely distributed of living species. (No. 3421, ×16 000)

Figure 25 *Rhabdosphaera claviger*, a modern species living in warm water. The large club-shaped stem is made of rhombohedral crystals drawn out into long fibres. (No. 2962, ×6000)

acid, and a transparent replica remains, with the surface detail picked out by shading. With the exception of figure 1, the illustrations of this article show replicas of this kind, shaded with chromium.

These illustrations give some idea of the range of structure to be seen in coccoliths of different species. In some species, the characteristic rhomb-shaped faces of calcite crystals are clearly visible (figures 5, 9, 16), but usually the shape of these crystals is modified (figures 4, 25), or even altered beyond recognition (figure 24). Indeed, it is apparent that the living cell has a very firm control over the shape of the calcite granules that it secretes, and can force the mineral to assume shapes very different from those of crystals grown inorganically, although we have no knowledge of the mechanism of this control. In addition, it also has a very exact control of the sites of nucleation, so that crystals are never found scattered at random within the cell or on its surface; they are always collected into orderly little clusters that form coccoliths. In some species, the arrangement of crystals within each cluster is quite simple (figures 18, 19, 23), but usually it is rather more elaborate (figures 6, 7) and is sometimes extraordinarily complicated (figures 8, 17). Most species with coccoliths of this kind have quite short ranges in geological time, and of those that are found living in the modern oceans, many are newly evolved forms with no known geological history. The species forming such coccoliths are easily identified, and can be very useful for dating rocks in the absence of larger fossils [5, 6].

In the great majority of coccoliths, the component crystals adopt the rhombohedral habit, in which none of the faces are at right angles [7]. When such crystals are crowded together to form a circular or elliptical rosette, their oblique interfacial angles cause them to override each other, like the tiles on a roof (figures 4, 9). For this reason, there is nearly always some rotary or spiral element in the architecture of coccoliths built out of rhombohedral crystals (figures 7, 8, 17).

The shape of the crystals, and the pattern of the coccoliths into which they are assembled, clearly result from a compromise between the tendency of calcite to shape itself into sharp-angled rhombohedra, and the ability of the living cell to control and even overrule this tendency. Recent work on the growth of coccoliths has given some indications of how the control works, but as yet very little evidence about the nature of the control itself. In the first place, it has been shown that the coccoliths are not formed at the surface of the cell, where they would be exposed to sea-water; they are prefabricated in special vacuoles deep within the interior, and only when growth is complete are they extruded to the surface. In some species, a very thin scale of organic matter is formed first of all, and calcite crystals are later caused to grow on its surface [2]; in other species, more elaborate matrices are developed at special places within the cell, and calcification takes place within each matrix under very precise control [8, 9].

Distribution of living species

Most coccolith-bearing algae live in the open ocean. Because of their dependence on light for photosynthesis, they are mainly concentrated in the top 100 metres of water. Many species, however, cannot tolerate the fierce sunlight that enters the water near the equator, and prefer to live at a depth where the light is more subdued. In the tropics, the maximum concentration is commonly at about 50 metres, whereas in temperate regions, as for example off the British Isles, it is more often between 10 and 20 metres [10–12]. In general, there are more individuals per litre in northern and southern waters than in those of the tropics. G. R. Hasle [10] found up to 32 000 per litre in the equatorial Pacific, as compared with over 360 000 farther south near the Antarctic Convergence. Samples taken in May from the sea north of Scotland commonly have between 50 000 and 100 000 cells per litre, with local concentrations of more than one million. These denser populations in high latitudes are mainly due to the great abundance of a few species, prominent among which is the ubiquitous *Coccolithus huxleyi* (figure 24). In tropical waters, on the other hand, there is a much greater variety of species, in spite of the smaller total number of cells per litre. For example, Hasle found 34 species in water samples from the equatorial Pacific,

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

whereas samples from the Sub-Antarctic contained only five, four of which were extremely rare, and were obviously strays [10].

Individual species differ considerably in their distribution throughout the oceans. *C. huxleyi* extends from the Arctic to the Antarctic, and is common in every ocean. A few other species, such as *C. leptoporus* and *Gephyrocapsa oceanica*, have nearly as wide a distribution. *Rhabdosphaera claviger* (figure 25), on the other hand, is abundant only in warm waters, such as the Mediterranean and the tropical parts of the Atlantic and Pacific oceans. *Coccolithus pelagicus* (figure 4), one of the first species to be discovered, has a peculiarly restricted distribution. It is apparently confined to the cool waters of the North Atlantic, and is not found south of the latitude of Portugal. Records from the Indian and Pacific oceans are unconfirmed, and all attempts to find it in waters of suitable temperature in the southern oceans have failed.

Not many species will tolerate a salt concentration much different from that of the open ocean; at salinities higher than 38 parts per thousand, or lower than 25, the number of species that can flourish is severely restricted. *Coccolithus huxleyi* can live in waters too dilute for other species, and has been found in canals with salinities as low as 15 parts per thousand [13]. A few freshwater species have been discovered. The best known of these is *Hymenomonas roseola*, which is sometimes quite abundant in freshwater lakes and ponds.

Quantitative studies of the plankton in sea-water have shown that coccospheres are capable of reaching enormous concentrations when conditions are particularly favourable. In May, there are normally between 50 000 and 100 000 cells of *C. huxleyi* per litre in the open Atlantic between the Faroes and Scotland. Water from this region drifts into the North Sea between the Shetlands and Norway, and some of this finds its way into the Skagerrak. During the journey, the population of *C. huxleyi* dwindles to about 5000 cells per litre, and less than this number at the entrance to the Oslo Fjord. In the early summer the water of the Oslo Fjord is thus inoculated with a small concentration of cells drawn in from the Atlantic; events during the later part of the summer vary from year to year. In some years, no spectacular proliferation takes place; in others, the water becomes discoloured, bathing becomes unpleasant, and the number of cells increases to several millions per litre. Statistics for one of these summers (1939) were collected by E. Birkenes and T. Braarud [14], who found that when the population density reached its peak between 2nd and 5th August there were more than 13 million cells per litre at the head of the fjord near Oslo. Such a concentration would hardly be possible without an unusually liberal supply of nutrients, and these are provided by the drainage from the harbour and the city.

The fossil record

Coccoliths are extremely abundant in many Mesozoic and Tertiary rocks, but their earlier history is virtually unknown. Although some of the earliest known species are rather simply constructed, others are quite elaborate, and must have had a fairly long evolutionary history behind them. For this reason it would be interesting to discover their ancestors in older rocks; but certain difficulties have up to the present prevented this. For instance, very small particles of calcium carbonate, such as those of which coccoliths are constructed, are apt to recrystallize if the enclosing rocks are subjected to heavy loading or to shearing stresses, and the characteristic shape of the coccolith is lost. Again, during the conversion of a marl into an argillaceous limestone, the growth of cementing crystals may so encrust the coccoliths that they become unrecognizable. In general, the older the rock, the greater the likelihood that it has suffered one or other of these changes, and the smaller the chance that any coccoliths it contains are still recognizable.

Key to the geological age of species illustrated

The beginning of each major division is dated in millions of years [4]

Living species: figures 4, 24, 25.
Upper Tertiary (26m. years): figures 22, 23
Lower Tertiary (65m. years): figures 17–21
Upper Cretaceous (100m. years):
  Chalk: figures 2, 3, 16
  Cambridge Greensand: figures 1, 13–15
Lower Cretaceous (136m. years):
  Gault (Albian): figures 9–12
  Sutterby Marl (Aptian): figure 8
Upper Jurassic (162m. years):
  Kimeridge Clay: figures 6–7
Lower Jurassic (190–195m. years):
  Lower Lias (Hettangian): figure 5

Samples of the oldest well-preserved coccoliths known in western Europe can be collected from marl-bands in the Lower Lias of the Dorset coast. *Alvearium* (figure 5) has a simple arrangement of rhombohedral crystals piled round a central axis to give a hemispherical or beehive-shaped coccolith; it is unknown from any strata later than the Lower Lias, and may be a survivor from some earlier period. Most of the associated species have a more complicated structure, and link up with types familiar in later rocks. The higher beds of the Oxford Clay are distinguished by an abundance of little wheel-shaped coccoliths, which G. Deflandre has named *Stephanolithion*; these survive, in decreasing numbers, into the Lower Cretaceous (figure 11). The commonest forms in the overlying Ampthill Clay have an unexpectedly modern appearance, as also have those of the Kimeridge Clay (figures 6, 7). C. Downie [15] found that at certain levels in the cliffs near Kimeridge in Dorset, coccoliths are so numerous (up to 95 per cent of the rock, equivalent to about 4 million per cubic millimetre) that they form thin beds of limestone, known as the White Stone Bands.

In the Lower Cretaceous, the commonest coccoliths (figure 12) differ from those of the Upper Jurassic in minor details only; at the same time, a number of new forms begin to appear (figure 8). They appear very sparingly at first, but increase in abundance up to the top of the Lower Cretaceous, where there is a remarkable diversity of species (figures 9–12). These are present in enormous numbers in the Gault Clay at Folkestone, and in clays of similar age elsewhere in the eastern counties of Britain.

The microstructure of the Cambridge Greensand, at the base of the Upper Cretaceous, was first studied by W. J. Sollas, who in 1876 remarked that its marly matrix 'is to a great extent composed of coccoliths, entire and fragmentary, which in the number and variety of forms surpass all that I have yet seen figured from recent seas'

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

[16]. The few examples illustrated here (figures 13–15) give but a poor idea of the great variety of forms discovered by Sollas, and more recently examined under the electron microscope. In the White Chalk there is less diversity of form than in the Gault or Cambridge Greensand, but the actual number of coccoliths per cubic millimetre is greater; indeed, chalk owes much of its lithological character to this exceptional abundance of coccoliths. Some species (figures 3, 16) are confined to particular subdivisions of the Chalk; others range through the whole formation from top to bottom (figure 2). One of these persistent species, *Deflandrius cretaceus* (figure 14) has a special importance in the constitution of chalk. Its coccoliths consist of 16 granules loosely held together in a ring, which easily disintegrates to release the individual granules, each about one micron in diameter. Innumerable particles of this size form the bulky white powder in which the other ingredients of chalk are embedded.

Most of the Cretaceous species appear to have had a span of existence equal to one or two of the stages into which the system is divided; in terms of years, this is equivalent to 5 to 10 million years, from their first appearance until they became extinct. *D. cretaceus* and a few other persistent forms flourished for about 35 million years before they died out at the end of the Cretaceous period. One species, *Braarudosphaera bigelowi* (figure 23), is unique in having survived from the Cretaceous through to the present day. It was found living in the Bay of Fundy in 1931, and has since been recorded just west of the English Channel, and at several other places in the North Atlantic.

The other Cretaceous coccoliths, almost without exception, became extinct at the end of the period, and a host of new species appeared in the Tertiary; some of these are remarkable for their large size or their bizarre shapes (figure 21). The outstanding feature of Tertiary assemblages, however, is the presence of an entirely extinct group of fossils, believed to be closely related to the coccoliths, and known as discoasters (figures 18–20); these are unknown from rocks of any other age. The earliest forms, at the base of the Tertiary, are mostly circular disks with a large number of rays. In the London Clay, which is slightly higher in the Lower Tertiary, three-rayed discoasters have been found, but species with 8–10 rays are more characteristic, and range up to the top of the Lower Tertiary (figures 18, 19), together with a number of six-rayed forms (figure 20). The Upper Tertiary is distinguished by an abundance of special six-rayed species, by which rocks of this age can be easily dated. With the first cold spell at the beginning of the Pleistocene ice age, the discoasters were all killed off, and not a single species survives.

Although it is probably true to say that the discoasters were finally exterminated by rapid chilling of the water in which they lived, there are reasons for thinking that the Ice Age merely dealt a *coup-de-grâce* to an already dying stock. Both the discoasters and the coccoliths appear to have been suffering a decline throughout the later part of Tertiary time, with one species following another to extinction, until only a few were left to face the rigours of the Ice Age. A few Tertiary species of coccoliths survived and are still living, but the great majority of those living in the present oceans are of very recent origin and have come into existence since the end of the Tertiary. Samples from the floor of the ocean show no record of a gradual evolution, and it is difficult to explain the suddenness with which so great a variety of new species made their appearance.

We know very little about the process of evolution in these primitive plants, among which sexual reproduction is unknown, but recent laboratory work with cultures has opened up several promising lines of inquiry. One possibility of explosive evolution may be seen in the complicated life-histories of many scale-bearing Chrysophyceae. As Mary Parke and Irene Manton have recently pointed out, if one of these algae lost its ability to run through the complete cycle of changes involved in its normal life-history, one stage might become fixed and perpetuate itself indefinitely. 'The resulting populations would become species, if able to establish themselves against the pressure of natural selection. Such developments, if they occurred, could be rapid, since complex sequences needing perhaps millennia to develop can certainly be stopped by single mutations. One species such as this is therefore potentially capable of explosive development into a cluster of species' [18].

This is an interesting possibility, but much more work will be needed to decide whether a process of this kind was, in fact, responsible for the repopulation of the oceans with these algae since the end of the Tertiary.

Acknowledgments

Most of the illustrations are from photographs taken at the Sedgwick Museum, Cambridge, by P. J. W. Hyde, using an Associated Electrical Industries EM6 electron microscope, provided by a grant from D.S.I.R. The prints are by Albert Barlow. The original of figure 1 was taken by the Cambridge Instrument Company, to whom I am much indebted for permission to reproduce it.

References

[1] Sorby, H. C. *Ann. Mag. nat. Hist.*, 3, (8), 194, 1861.
[2] Parke, M. and Adams, I. *J. mar. biol. Ass. U.K.*, 39, 263, 1960.
[3] Parke, M. *Br. phycol. Bull.*, 2, 47, 1961.
[4] Harland, W. B., Smith, A. G., and Wilcock, B. 'The Phanerozoic Time-scale'. Geological Society, London. 1964.
[5] Stradner, H. *Sixth World Petroleum Congress*, Paper 4, 1963.
[6] *Idem. Erdöl-Z.*, 4, 133, 1964.
[7] Black, M. *Proc. Linn. Soc. Lond.*, 174, 41, 1963.
[8] Paasche, E. *Physiologia Pl. Suppl.*, 3, 1, 1964.
[9] Wilbur, K. M. and Watabe, N. *Ann. N.Y. Acad. Sci.*, 109, 82, 1963.
[10] Hasle, G. R. *Nytt Mag. Bot.*, 8, 77, 1960.
[11] Halldal, P. *Hvalrådd. Skr.*, 38, 1, 1953.
[12] Braarud, T., Gaarder, K. R., and Grøntved, J. *Rapp. Cons. Explor. Mer.* 133, 1–87, 1958.
[13] Schiller, J. 'Coccolithineae' in 'Rabenhorst's Kryptogamen-Flora', 10 (2), 89, 1930.
[14] Birkenes, E. and Braarud, T. *Avh. norske VidenskAkad. Oslo*, No. 2, 1–23, 1952.
[15] Downie, C. *Q. Jl geol. Soc. Lond.*, 112, 413, 1957.
[16] Sollas, W. J. *Geol. Mag.*, 13, 539, 1876.
[17] Martini, E. *Erdöl Kohle*, 12, 137, 1959.
[18] Parke, M. and Manton, I. *J. mar. biol. Ass. U.K.*, 42, 391, 1962.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

The fluorides of nitrogen

Digitized by Arya Samaj Foundation Chennai and eGangotri

Charles B. Colburn

The first fluoride of nitrogen was made nearly forty years ago, but this synthesis did not immediately lead to many others. Recently, a large number of compounds containing a nitrogen-fluorine bond have been made and examined. This article describes the preparation and properties of some of these compounds, both inorganic and organic, and suggests some possible future uses.

The element fluorine has been involved in at least two of the more significant recent developments in inorganic chemistry. N. Bartlett has recently given an account of one of these developments—the chemistry of the noble gases—for ENDEAVOUR [1]; we shall review here a second —that of the fluorides of nitrogen.

Although the first attempt to prepare a fluoride of nitrogen was described by O. Ruff in 1903, he was unable to report a successful preparation until 1928 [2]; the actual compound was nitrogen trifluoride, NF_3. Thirty years after Ruff's discovery of NF_3, there still was a total of only three inorganic molecules containing the N—F bond: NF_3 [2], and N_2F_2 and FN_3 [3]. In 1958, C. B. Colburn and A. Kennedy first reported [4] the synthesis of tetrafluorohydrazine (N_2F_4). In the six years since that discovery, approximately one hundred and fifty papers have been published covering the synthesis, structure, and bonding of numerous compounds, both inorganic and organic, containing the nitrogen-fluorine (N—F) bond. Some of these recently synthesized compounds are: difluoramine (HNF_2), nitrosodifluoramine ($ONNF_2$), chlorodifluoramine ($ClNF_2$), dichlorofluoramine (Cl_2NF), the difluoramino free radical ($\cdot NF_2$)[1], difluoramino sulphur pentafluoride (SF_5NF_2), N,N-difluoromethylamine (CH_3NF_2), N,N-difluorourea ($H_2N{-}\overset{\overset{O}{\|}}{C}{-}NF_2$), and N-fluoro-N′-trifluoromethyldiazine N′-oxide ($CF_3{-}\overset{\overset{O}{\uparrow}}{N}{=}NF$).

These developments are of significance to the synthetic inorganic and organic chemist, and also to the physical chemist. This is because the synthesis of a series of new simple molecules, and especially of a series containing a new type of chemical bond, occurs only infrequently. The structural and theoretical chemist, as well as the spectroscopist, are delighted when such a series does appear, since it provides them with new compounds on which to test their structural and bonding theories. Numerous papers containing theoretical and structural studies of these N—F compounds have appeared since 1958.

At first glance, it is tempting to consider the various compounds containing the nitrogen-fluorine bond to be derivatives of nitrogen trifluoride. However, the difluoramino free radical is so stable that it may be considered to be the parent molecule of this new group.

The tetrafluorohydrazine-difluoramino free radical system

Tetrafluorohydrazine (N_2F_4) was first prepared by the reaction of nitrogen trifluoride with copper packing in a hot tube at 350–400°C [4]. It was observed somewhat later [5] that tetrafluorohydrazine existed in a dissociative equilibrium with the difluoramino free radical:

$$N_2F_4 \rightleftharpoons 2 \cdot NF_2 \qquad \ldots.(1)$$

The difluoramino radical is quite stable and is capable of existing indefinitely in the free state. This behaviour is very similar to that shown by nitrogen dioxide, which exists in equilibrium with dinitrogen tetroxide:

$$N_2O_4 \rightleftharpoons 2 \cdot NO_2 \qquad \ldots.(2)$$

The behaviour of these two free radicals, $\cdot NO_2$ and $\cdot NF_2$, is quite different from that of the amino free radical ($\cdot NH_2$). Hydrazine (N_2H_4) is thought to dissociate upon heating to high temperatures into two amino free radicals:

$$N_2H_4 \rightleftharpoons 2 \cdot NH_2 \qquad \ldots.(3)$$

However, these amino radicals are extremely reactive, and the end products of the hydrazine dissociation are in general ammonia, nitrogen, and hydrogen.

One explanation for the difference in the behaviour of the difluoramino and the amino free radicals lies in the difference between the order of the bond strengths in ammonia and that in nitrogen trifluoride. In ammonia, the first N—H bond is the strongest of the three N—H bonds; in nitrogen trifluoride, the first N—F bond is the weakest of the three N—F bonds (table 1).

One can assume that the N—H bond strengths in hydrazine are the same as those in NH_2 (88 kcal/mole), and that the N—F bond strengths in tetrafluorohydrazine are the same as those in NF_2 (71 kcal/mole). The tendency, due to energy considerations, for NH_2 to abstract a hydrogen atom from hydrazine or from the amino free radical to form ammonia is then obvious, and the inability of NF_2 to abstract F from NF_2 or N_2F_4 to form nitrogen trifluoride also becomes clear.

There are three reasons why the dissociative equilibrium of N_2F_4 can be readily investigated:

1. The difluoramino free radical absorbs light in the ultraviolet region of the spectrum (figure 1). The absorption is so intense that, even though N_2F_4 is dissociated only to an extent of a fraction of one per cent at room

[1] The definition of 'free radical' is at present rather vague. For our purposes, a free radical will be defined as being an uncharged atom or group of atoms containing an electron (in an *s*- or *p*-orbital) with unpaired spin. Frequently the electron with the unpaired spin is designated by a dot, as in the formula for the difluoramino free radical ($\cdot NF_2$).

Charles B. Colburn, *B.S., Ph.D.*

Was born in Harrisonville, Missouri, in 1923, and educated at Kansas State University and the University of Utah. Since 1952 he has been a Group Leader in physical chemistry at Rohm and Haas Company, Redstone Research Division, Huntsville, Alabama. His particular research interests are the physical chemistry of combustion and ignition, and the chemistry of nitrogen and fluorine.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Table I (D = dissociation energy)

$D(H_2N—H)$	104 kcal/mole [6]	$D(F_2N—F)$	57 kcal/mole [7]
D(HN—H)	88 kcal/mole	D(FN—F)	71 kcal/mole
D(N—H)	88 kcal/mole	D(N—F)	71 kcal/mole

temperature and atmospheric pressure, this ultraviolet absorption is easily observed under these conditions.

2. Since nitrogen difluoride (difluoramino) is a free radical, it possesses an electron with an uncoupled spin. This makes it readily detectable by means of epr (electron paramagnetic resonance) spectroscopy [8]. This provides a ready means of studying the equilibrium. The variation of the amplitude of this epr signal as a function of temperature is illustrated in figure 2.
3. Difluoramino free radical and tetrafluorohydrazine are relatively unreactive toward glass at temperatures up to those at which the dissociation of N_2F_4 is almost complete [5]. This makes the study of the pressure increase in the $N_2F_4 \rightleftharpoons 2 \cdot NF_2$ system (that is, the deviations from the pressure increases expected of a perfect gas) as a function of temperature convenient to investigate. All three of these methods give essentially the same value for the $F_2N—NF_2$ bond dissociation energy (19·8 kcal/mole).

The stable existence of the difluoramino free radical was first reported only in late 1960 [9], but it has been studied intensively since then, and we know perhaps more about this species than we do of any other radical. The studies include investigations of the ultraviolet [5] and infra-red [10, 11] absorption spectra, the mass cracking pattern, and the thermodynamic functions [11] of $\cdot NF_2$, and also the electronegativity of the NF_2 group in its various compounds [12].

One particularly interesting aspect of this radical is its epr spectrum. As figure 2 shows, the epr spectrum of the radical in the gas phase is a singlet. However, the theory of epr spectroscopy tells us that, if this spectrum were properly resolved, it should show nine lines. The coupling of the spin of the free electron with the spin of the nitrogen nucleus should give rise to three lines, and each of these should be split into a triplet by the further interaction of the spin of the electron with the nuclei of the two fluorine atoms. The fully resolved nine-line spectrum can be observed when $\cdot NF_2$ free radicals are adsorbed on Linde Molecular Sieve 5A (figure 3). The lack of hyperfine structure in the gas-phase spectrum is almost certainly due to rapid recombination.

Many of the reactions of tetrafluorohydrazine are due to the ease of its dissociation into $\cdot NF_2$ radicals and to the stability of the radicals themselves.

Nitrosodifluoramine ($ONNF_2$)

The tendency for free radicals to couple with one another in order to pair the spins of their free electrons to form chemical bonds is well known. Nitric oxide is a stable free radical, which at either low temperature or high pressure, or both, can couple with difluoramino free radicals to form nitrosodifluoramine [13]:

$$\cdot NF_2 + \cdot NO \rightleftharpoons ONNF_2 \qquad \ldots . (4)$$

The apparatus illustrated in figure 4 can be used in

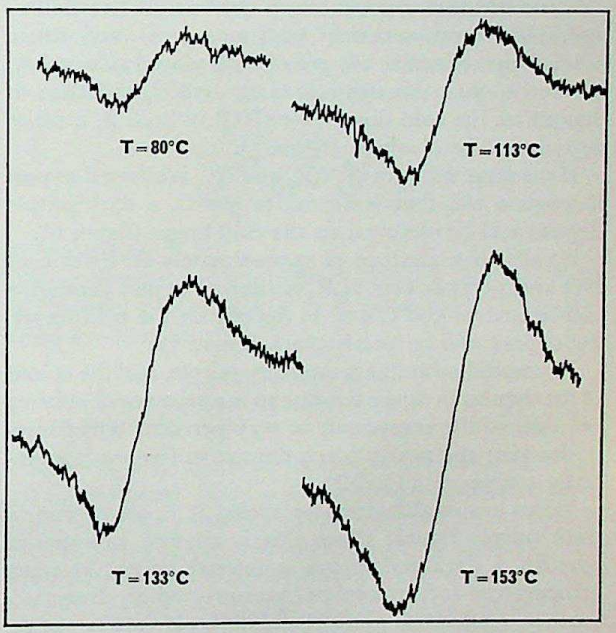


Figure 2 The influence of temperature on the electron paramagnetic resonance spectrum of $\cdot NF_2$.

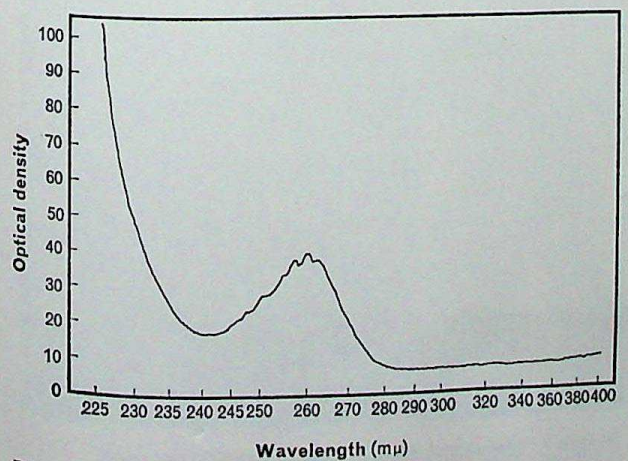


Figure 1 The ultraviolet absorption spectrum of the difluoramino free radical.

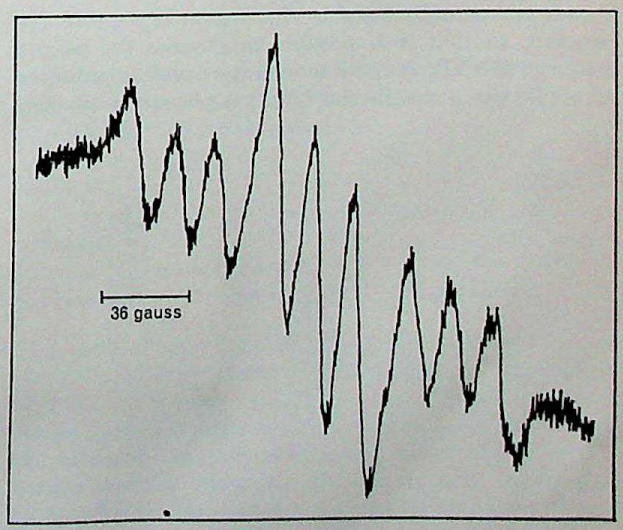


Figure 3 The nine-line derivative epr spectrum of NF_2 on molecular sieve 5A.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Table II

	Coil temperature (°C)	Percentage composition of gas in bulb	Percentage composition of gas in coil	Percentage composition of solid deposit on cold finger at −198°C
1		N_2F_4+·NO →	N_2F_4+·NO →	N_2F_4+N_2O_2[1]
	−78	99·4 0·6	99·4 0·6	99·7 0·3
2		N_2F_4+·NO →	·NF_2+·NO →	N_2F_4+$ONNF_2$
	300	99·4 0·6	99·7 0·3	99·4 0·6
3		N_2F_4+·NO →	·NF_2+·NO →	$ONNF_2$
	300	33·3 66·6	50 50	100

[1] At −198°C, even the relatively stable ·NO radical dimerizes to colourless N_2O_2.

three experiments (table II) to demonstrate the mode of formation of nitrosodifluoramine.

If, in the first experiment, a mixture of tetrafluorohydrazine (approximately 99·6 per cent) and nitric oxide (approximately 0·4 per cent) is placed in vessel A, allowed to pass through coil C at −78°C, and then to deposit on the cold finger (−198°C) in bulb B, a white deposit will be observed (figure 5).

If the same mixture of N_2F_4 and NO is allowed to pass through a coil that is heated to 300°C, a dark purple deposit will be observed on the cold finger (figure 6).

Finally, if a mixture of approximately 66·6 per cent NO and 33·3 per cent N_2F_4 is allowed to pass through a coil heated to 300°C and to deposit on the cold finger, the deposit will be nearly black (figure 7).

Nitrosodifluoramine is intensely purple, and the colour of the deposit in figure 6 is due to the presence of only 0·4 per cent of the compound in 99·6 per cent tetrafluorohydrazine; the nearly black deposit in figure 7 is essentially 100 per cent $ONNF_2$.

When nitrosodifluoramine melts, it is an extremely dark purple liquid. When this is allowed to vaporize rapidly, a dark purple gas is formed which, at room temperature and atmospheric pressure, rapidly dissociates into a colourless gaseous mixture of nitric oxide, tetrafluorohydrazine, and difluoramino free radical:

$$N_2F_4+2\cdot NO \rightleftharpoons 2\cdot NF_2+2\cdot NO \rightleftharpoons 2ONNF_2(\text{purple}) \ldots . (5)$$

The equilibrium involved in this system is pressure dependent, so that it is possible to observe the purple colour of $ONNF_2$ at room temperature and at pressures of about ten atmospheres. The gas-phase equilibrium

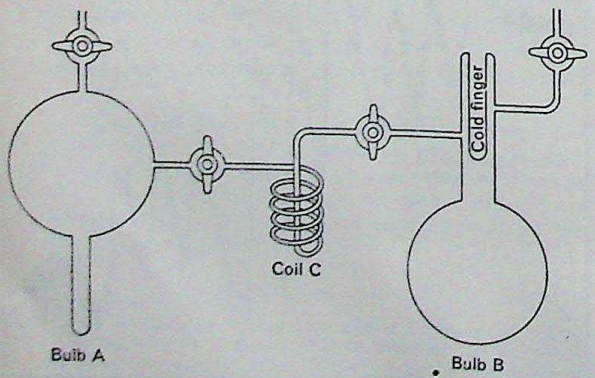


Figure 4 Apparatus for preparation of nitrosodifluoramine, F_2NNO.

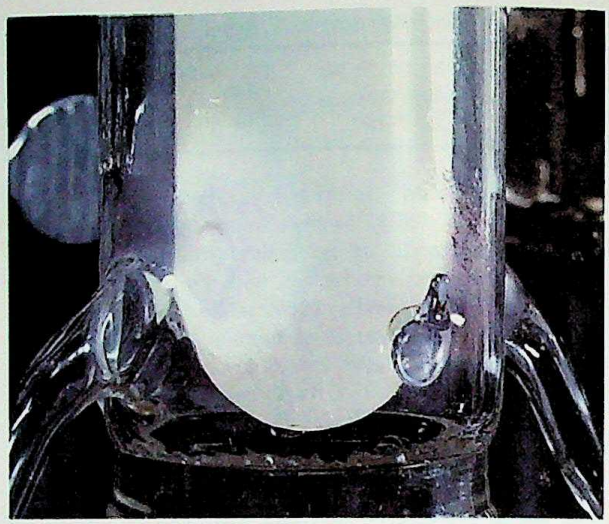


Figure 5 Deposit of 99·7 per cent tetrafluorohydrazine and 0·3 per cent nitric oxide dimer.

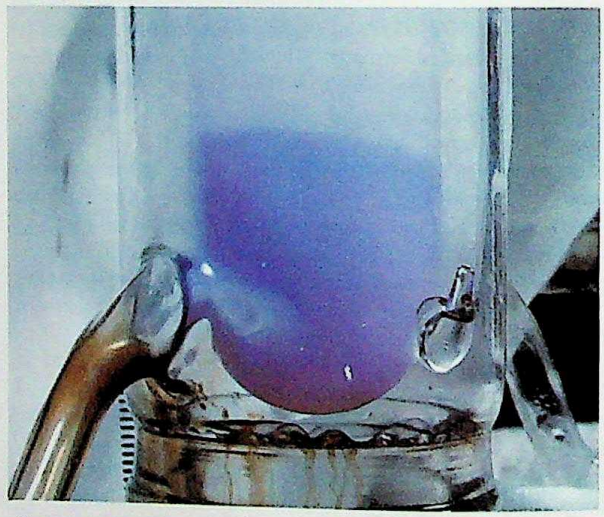


Figure 6 Deposit of 99·6 per cent tetrafluorohydrazine and 0·4 per cent nitrosodifluoramine.

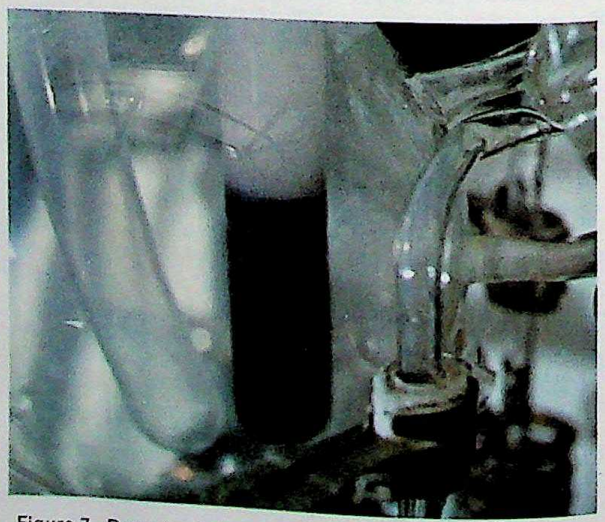


Figure 7 Deposit of nitrosodifluoramine (100 per cent).

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

between these species has been investigated and the heat of dissociation of the ON—NF_2 bond found to be approximately 10 kcal/mole [14].

Other derivatives of the difluoramino free radical

Difluoramine (HNF_2)

HNF_2 was first reported by Ruff in 1931 [18], but this was an error; the first authentic sample was prepared in 1959 by Kennedy and Colburn [19]. Several of the preparations of difluoramine appear to depend upon the removal of labile hydrogen atoms from compounds by the difluoramino free radical. For example, mercaptans, which are known to contain labile hydrogen atoms, react with tetrafluorohydrazine—actually with the dissociation product $\cdot NF_2$—to yield difluoramine (HNF_2) [15], and mercapto free radicals. These then couple to form organic disulphides:

$$N_2F_4 \rightleftharpoons 2 \cdot NF_2$$
$$2 \cdot NF_2 + 2RSH \rightarrow 2HNF_2 + 2RS\cdot$$
$$2RS\cdot \rightarrow RSSR$$

(R represents an alkyl radical.)

Another preparation of difluoramine is the reaction of arsine (AsH_3) with N_2F_4 to yield arsenic and difluoramine

$$AsH_3 + 1\tfrac{1}{2}\ N_2F_4 \rightarrow As + 3HNF_2$$

Other syntheses of difluoramine which do not necessarily involve free radicals include:

1. The reaction between trityl difluoramine and concentrated sulphuric acid [16]:

$$(C_6H_5)_3CNF_2 \xrightarrow{H^+} (C_6H_5)_3C^+ + HNF_2$$

2. The fluorination of urea at 0°C [17], which gives difluoramine in yields of 15 per cent.

Chlorodifluoramine ($ClNF_2$)

The original preparation of chlorodifluoramine by R. C. Petry [20] used the thermal decomposition of the Lewis acid complex of HNF_2 with boron trichloride. This did not necessarily involve free radicals. However, the other preparations almost certainly do. These are the photochemical equilibrium between chlorine, tetrafluorohydrazine, and chlorodifluoramine reported by Petry:

$$Cl_2 + N_2F_4 \overset{u.v.}{\rightleftharpoons} 2NF_2Cl$$

and the preparation by T. A. Austin and R. W. Mason; they propose in part the following mechanism [21]:

$$Cl + \cdot N_3 \rightarrow ClN_3$$
$$ClN_3 \rightarrow [ClN] + N_2$$
$$[ClN] + F_2 \rightarrow ClNF_2$$

Dichlorofluoramine (Cl_2NF)

The preparation of dichlorofluoramine by B. Sukornick, R. F. Stahl, and J. Gordon uses the reaction of sodium azide with chlorine monofluoride at 0°C [22]. It has been formulated as a free-radical reaction:

$$NaN_3 + ClF \rightarrow ClN_3 + NaF$$
$$ClN_3 \rightarrow [ClN] + N_2$$
$$[ClN] + ClF \rightarrow Cl_2NF$$

N,N-Difluorohydroxylamine-O-fluorosulphonate (NF_2OSO_2F)

F. B. Dudley and G. H. Cady have recently published a study [23] of the relative stability of the fluorosulphonate free radical and its equilibrium with peroxydisulphuryl difluoride. Some of this work has been anticipated by M. Lustig and G. H. Cady in their preparation of N,N-difluorohydroxylamine-O-fluorosulphonate by the thermal reaction of tetrafluorohydrazine and peroxydisulphuryl difluoride [24]. The equilibria can be expressed as follows:

$$FSO_2O—OSO_2F \rightleftharpoons 2FSO_2O\cdot$$
$$N_2F_4 \rightleftharpoons 2 \cdot NF_2$$
$$\cdot NF_2 + FSO_2O\cdot \rightarrow FSO_2ONF_2$$

Difluoramino sulphur pentafluoride (SF_5NF_2)

It has been proposed that the thermal decomposition of disulphur decafluoride into sulphur hexafluoride and sulphur tetrafluoride takes place by a chain mechanism, the first step of which is the dissociation of S_2F_{10} into two $\cdot SF_5$ radicals. Two groups of investigators have studied the thermal reaction between disulphur decafluoride and tetrafluorohydrazine at 150°C and have obtained difluoramino sulphur pentafluoride, SF_5NF_2, as a product. The following mechanism is suggested:

$$S_2F_{10} \rightleftharpoons 2 \cdot SF_5$$
$$N_2F_4 \rightleftharpoons 2 \cdot NF_2$$
$$\cdot SF_5 + \cdot NF_2 \rightarrow SF_5NF_2$$

Difluorodiazine (N_2F_2)

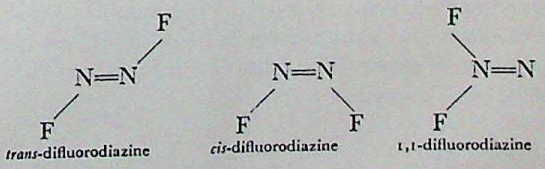
Difluorodiazine was first prepared by J. F. Haller [3] by the thermal decomposition of fluorine azide. The proposed reaction scheme is:

$$FN_3 \rightarrow [FN:] + N_2$$
$$2[FN:] \rightarrow FN{=}NF$$

Recently the photochemical decomposition of N_2F_4 was investigated [25], and the major products were found to be NF_3 and N_2F_2. This reaction is best understood in terms of the decomposition of the electronically excited difluoramino free radical ($\cdot NF_2{}^*$) as follows:

$$N_2F_4 \rightleftharpoons \cdot NF_2 \xrightarrow{h\nu} \cdot NF_2{}^*$$
$$\downarrow$$
$$NF_3 \xleftarrow{\cdot NF_2} \cdot F + [:NF]$$
$$\downarrow$$
$$N_2F_2$$

Difluorodiazine is itself an interesting molecule. The three following isomeric structures would appear to be possible for such a compound:



The *cis* and *trans* isomers arise since rotation about a double bond is not permitted. Two isomeric forms of this material have been isolated to date. There has been considerable discussion of their structure, but the bulk of the evidence—mass spectrometric, electron diffraction, double nuclear magnetic resonance, and microwave spectra—indicates that they are the cis and trans forms. The synthesis, and identification, of the third isomer are awaited with great interest.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Organic derivatives of the difluoramino free radical

Although free-radical studies have historically been mainly in organic chemistry, most of the reactions described above are inorganic. However, a wealth of organic reactions involving the difluoramino free radical have been described.

J. W. Frazer found [26] that both methyl and ethyl iodide react in ultraviolet light with tetrafluorohydrazine to form principally N,N-difluoroalkyl amines. The following reaction sequence is suggested:

$$C_2H_5I \xrightarrow{u.v.} C_2H_5\cdot + I$$
$$N_2F_4 \rightleftharpoons 2 \cdot NF_2$$
$$C_2H_5\cdot + \cdot NF_2 \rightarrow C_2H_5NF_2$$

R. C. Petry and J. P. Freeman have found [27] that the photolysis of diketones in the presence of tetrafluorohydrazine at room temperature resulted in the formation of N,N-difluoramides in high yields. The suggested mechanism is:

$$R{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow{h\nu} 2R{-}\overset{O}{\overset{\|}{C}}\cdot$$

$$R{-}\overset{O}{\overset{\|}{C}}\cdot + \cdot NF_2 \rightarrow R{-}\overset{O}{\overset{\|}{C}}{-}NF_2$$

Alkyl radicals generated in other ways, such as by decomposition of azo-iso-butyronitrile, azo-t-butane, or hexaphenylethane, also reacted with $N_2F_4(NF_2)$ to produce the corresponding difluoramines:

$$(CH_3)_2{-}\overset{CN}{\overset{|}{C}}{-}NF_2, \quad (CH_3)_3{-}CNF_2, \quad (C_6H_5)_3{-}C{-}NF_2$$

N,N-difluoramides may also be obtained by the reaction of aldehydes with N_2F_4. The reaction probably takes place by removal of hydrogen followed by coupling of the radicals:

$$CH_3\overset{O}{\overset{\|}{C}}{-}H + \cdot NF_2 \rightarrow CH_3{-}\overset{O}{\overset{\|}{C}}\cdot + HNF_2$$

$$CH_3\overset{O}{\overset{\|}{C}}\cdot + \cdot NF_2 \rightarrow CH_3\overset{O}{\overset{\|}{C}}{-}NF_2$$

Frazer has recently reported a new class of organic NF compounds, N-fluoroazoxy compounds [28]. Trifluoronitrosomethane reacts with $N_2F_4(NF_2)$ under the influence of heat or ultraviolet light to form N-fluoro-N′-trifluoromethyldiazine-N′-oxide. The following mechanism was proposed:

$$CF_3NO + \cdot NF_2 \rightarrow CF_3\overset{O}{\overset{\uparrow}{N}}{=}NF + \cdot F$$

Uses of NF Compounds

While there are no commercial uses of these compounds known to the author, several suggestions have been made. Thus H. H. Rogers has suggested the use of nitrogen trifluoride with hydrogen in a torch [29]. The torch could weld and braze metals without additional flux, as the nitrogen trifluoride acts as a gaseous flux. Colburn's observation [30] that difluorodiazine is a gaseous catalyst for the polymerization of various monomers is interesting, in that J. F. Smith and J. R. Albin have recently studied [31] the vulcanization of fluoroelastomers with difluorodiazine. In addition, C. S. Cleaver has reported [32] that N_2F_4 acts as an initiator in free-radical chain reactions and may be used as a polymerization catalyst.

Conclusion

The synthesis of tetrafluorohydrazine and the discovery of the ease of dissociation of the compound into difluoramino free radicals has opened new areas of investigation in inorganic, organic, and polymer chemistry. Since this is a relatively new field of chemistry, the ultimate usefulness of the many possible derivatives of the difluoramino free radical is unknown and essentially uninvestigated.

Acknowledgment

This work was carried out under Army Contract No. DA-01-021 ORD-11878(Z). The author wishes to express his appreciation to the following for use of figures in this paper: Figure 1, Butterworth's 'Advances in Fluorine Chemistry', Vol. 3; Figure 2, American Institute of Physics, (*J. chem. Phys.*, 35, 1481, 1961); Figure 3, American Chemical Society, (*Inorganic Chemistry*, 3, 456, 1964).

References

[1] Bartlett, N. *Endeavour*, 23, 3, 1964.
[2] Ruff, O., Fischer, J., and Luft, F. *Z. anorg. Chem.*, 172, 417, 1928.
[3] Haller, J. F. Ph.D. Thesis, Cornell University, 1942.
[4] Colburn, C. B. and Kennedy, Al. *J. Am. chem. Soc.*, 80, 5004, 1958.
[5] Johnson, F. A. and Colburn, C. B. *Ibid.*, 83, 3043, 1961.
[6] Altshuller, A. P. *J. chem. Phys.*, 22, 1947, 1954.
[7] Kennedy, A. and Colburn, C. B. *Ibid.*, 35, 1892, 1961.
[8] Piette, L. H., Johnson, F. A., Booman, K. A., and Colburn, C. B. *Ibid.*, 35, 1481, 1961.
[9] Colburn, C. B. and Johnson, F. A. *Ibid.*, 33, 1869, 1960.
[10] Johnson, F. A. and Colburn, C. B. *Inorg. Chem.*, 1, 431, 1962.
[11] Harmony, M. D. and Myers, R. J. *J. chem. Phys.*, 37, 636, 1962.
[12] Ettinger, R. *J. Phys. Chem.*, 67, 1558, 1963.
[13] Colburn, C. B. and Johnson, F. A. *Inorg. Chem.*, 1, 715, 1962.
[14] Johnson, F. A. and Colburn, C. B. *Ibid.*, 2, 24, 1963.
[15] Freeman, J. P., Kennedy, A., and Colburn, C. B. *J. Am. chem. Soc.*, 82, 5304, 1960.
[16] Graham, W. H. and Parker, C. O. *J. org. Chem.*, 28, 850, 1963.
[17] Lawton, E. A. and Weber, J. Q. *J. Am. Chem. Soc.*, 81, 4755, 1959.
[18] Ruff, O. and Stauh, L. *Z. anorg. Chem.*, 198, 32, 1931.
[19] Kennedy, A. and Colburn, C. B. *J. Am. Chem. Soc.*, 81, 2906, 1959.
[20] Petry, R. C. *Ibid.*, 82, 2400, 1960.
[21] Austin, T. A. and Mason R. W. *Inorg. Chem.*, 2, 646, 1963.
[22] Sukornick, B., Stahl, R. F., and Gordon, J. *Ibid.*, 2, 875, 1963.
[23] Dudley, F. B. and Cady, G. H. *J. Am. Chem. Soc.*, 85, 3375, 1963.
[24] Lustig, M. and Cady, G. H. *Inorg. Chem.*, 2, 388, 1963.
[25] Bumgardner, C. L. and Lustig, M. *Ibid.*, 2, 662, 1963.
[26] Frazer, J. W. *J. inorg. nucl. Chem.*, 16, 63, 1960.
[27] Petry, R. C. and Freeman, J. P. *J. Am. Chem. Soc.*, 83, 3912, 1961.
[28] Frazer, J. W., Holder, B. E., and Worden, B. F. *J. inorg. nucl. Chem.*, 24, 45, 1962.
[29] Rogers, H. H. *Ind. Engng Chem.*, 51, 309, 1959.
[30] Colburn, C. B., Johnson, F. A., Kennedy, A., McCallum, K. Metzger, L. C., and Parker, C. O. *J. Am. Chem. Soc.*, 81, 6397, 1959.
[31] Smith, J. F. and Albin, J. R. *Ind. Engng Chem., Prod. Res. Dev.* 2, 284, 1963.
[32] Cleaver, C. S. (to E. I. du Pont de Nemours & Co. Inc.), U.S. Patent 2,963,468 (6 Dec. 1960).

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

ACS RESEARCH JOURNALS

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Since its founding in 1876 the American Chemical Society has placed publishing among its major functions. ACS journals have presented high quality research reports for the professional chemist, all accepted for publication after careful refereeing, all edited with the highest standards. In the past decade the Society's publishing program has expanded rapidly in response to member demand for outlets for each of the classical fields of chemistry as well as certain subspecialties. Additional journals are likely to appear in the future.

This booklet describes briefly the 12 research journals produced by the American Chemical Society in 1965 and gives their prices. They may be ordered easily through the use of the form on the last page of this booklet.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Founded in 1879, JACS is the oldest ACS publication. Its papers are from basic work in organic, physical, inorganic, and biological chemistry. They are accepted only if they cut across more than one field or provide material in a specialized area of such fundamental interest as to appeal to everyone engaged in research in basic chemistry.

In addition to some 40 papers per issue, JACS offers Communications to the Editor, preliminary reports of unusual significance or urgency. In 1964 there were 608 Communications published in JACS. This journal also presents book reviews.

JACS is issued in 24 semimonthly numbers and in 1965 will publish some 5,000 pages.

Editor: *Dr. Marshall D. Gates, Jr.*

1 year: *ACS members* *$13.00*
All others *26.00*

Postage: *Foreign $3.50; PUAS and Canada $2.50*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

JOURNAL OF ORGANIC CHEMISTRY

Started in 1936, this monthly journal is the leading American journal devoted to general organic chemistry. Its papers are comprehensive and critical accounts of original work in a given area of organic chemistry or interpretive reviews of existing data which present new viewpoints.

JOC presents some 60 papers per issue plus Notes, brief, concise accounts of studies of smaller scope.

Editor-in-Chief: *Dr. Frederick D. Greene*

Senior Editors: *Dr. Glenn A. Berchtold*
Dr. Werner Herz
Dr. James A. Moore

1 year: *ACS members* $12.50
All others 25.00

Postage: *Foreign $3.50; PUAS and Canada $2.50*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

JOURNAL OF PHYSICAL CHEMISTRY

JPC is the only basic journal in the United States devoted to general physical chemistry. It is the second oldest such journal in the world.

Editorial philosophy was recently broadened to include theoretical as well as experimental papers.

Each month JPC presents some 50 articles on all phases of physical chemistry, including important symposia from the ACS Division of Colloid and Surface Chemistry. Many papers come from laboratories abroad; an arrangement with the Faraday Society of London facilitates their reception and screening.

Editor: *Dr. Frederick T. Wall*

1 year: *ACS members* *$12.00*
All others *24.00*

Postage: *Foreign $3.00; PUAS and Canada $2.00*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

BIOCHEMISTRY

Founded in 1962, BIOCHEMISTRY has expanded from bi-monthly to monthly publication in three years' time. In 1965 it is scheduled to publish some 2,400 pages.

Papers reflect results of original research in all recognized or developing areas of fundamental biochemistry. The journal emphasizes investigations that generate new concepts and experimental approaches.

Manuscripts are published, on an average, three and a half months after acceptance. BIOCHEMISTRY offers some 25 papers in each issue.

Editor: *Dr. Hans Neurath*

1 year: *ACS members* *$13.00*
All others *26.00*

Postage: *Foreign $1.50; PUAS and Canada $1.00*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

JOURNAL OF MEDICINAL CHEMISTRY

This recently founded bimonthly journal offers the reader unusual value in that articles describing compounds are not accepted unless the biological data accompany the chemistry. Subject matter includes the structural elucidation, chemistry, preparation and physical properties of biologically significant materials, their structure-activity relationships, the transport and metabolism of drugs, and the action of medicinal agents.

Where biological data are lacking, a special feature, "New Compounds," gives the briefest of descriptions of the synthesis of analogs of known drug structures.

JMC also publishes Notes and Book Reviews.

Editor: *Dr. Alfred Burger*

1 year: *ACS members* $10.00
All others 20.00

Postage: *Foreign $1.50; PUAS and Canada $1.00*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

INORGANIC CHEMISTRY

Since its inception in 1962 this new journal has evolved rapidly from quarterly to monthly publication, and now accounts for 2,000 pages yearly.

Its articles may range in content from the borders of organic chemistry to the borders of theoretical physics. Subject matter includes synthesis and properties of new compounds, quantitative studies regarding structure, and thermodynamies and kinetics of inorganic reactions.

Aside from some 30 papers in each issue, INORGANIC CHEMISTRY presents Notes, Book Reviews, and a special section called Correspondence, informally reporting results or scientific views.

Editor: *Dr. Edward L. King*

1 year: *ACS members* *$11.00*
All others *22.00*

Postage: *Foreign $1.50; PUAS and Canada $1.00*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

INDUSTRIAL AND ENGINEERING CHEMISTRY QUARTERLIES

These journals publish reports of original work in chemical process design and development, in the theoretical or fundamental aspects of chemical engineering, and in chemical products research and development.

I&EC PROCESS DESIGN AND DEVELOPMENT reports on design methods and concepts and their application to the development of processes and process equipment.

I&EC FUNDAMENTALS publishes papers in the broad field of chemical engineering research. No technical field to which important contributions are being made is excluded—whether experimental or theoretical, mathematical or descriptive, chemical or physical.

I&EC PRODUCT RESEARCH AND DEVELOPMENT publishes papers reporting findings on the preparation of new or improved chemical products, as well as findings on improved methods for the preparation of existing products.

Research quarterly editors:
Process Design and Development—*Dr. Hugh M. Hulburt*
Fundamentals—*Dr. Robert L. Pigford*
Product Research and Development—*Rodney N. Hader (acting editor)*

1 year:

	1 Quar. and I&EC.		*2 Quar. and I&EC*		*3 Quar. and I&EC*	
ACS	*Domestic and Canada*	*Foreign*	*Domestic and Canada*	*Foreign*	*Domestic and Canada*	*Foreign*
members	$4.00	$ 4.00	$7.00	$ 7.00	$10.00	$10.00
All others	5.00	13.00	8.50	17.50	12.00	22.00

Postage: *One quarterly plus I&EC*
Foreign: $2.50; PUAS and Canada $1.50
Two quarterlies plus I&EC
Foreign: $3.00; PUAS and Canada $2.00
Three quarterlies plus I&EC
Foreign: $3.50; PUAS and Canada $2.50

Note: *Separate subscriptions to either the monthly or the quarterlies will not be accepted.*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

ANALYTICAL CHEMISTRY

This monthly is the only complete and authoritative source of technical information covering all fields of analysis, both fundamental and applied. Articles, whether staff-written or contributed, are intended to meet the needs of those engaged in theoretical analytical research and those developing practical analytical methods, procedures, and techniques.

The material is assembled in categories, such as AC Briefs, summaries of papers presented in the technical section; Scientific Communications, new analytical developments; Correspondence; Aids for the Analyst; the Report for Analytical Chemists; Book Reviews; Laboratory of the Month; Instrumentation; New Products; New Chemicals.

Editor: *Dr. Lawrence T. Hallett*

		Domestic and Canada	*Foreign*
1 year:	*ACS members*	$ 4.00	$ 4.00
	All others	5.00	15.00
2 years:	*ACS members*	7.00	7.00
	All others	9.00	27.50
3 years:	*ACS members*	10.00	10.00
	All others	12.00	40.00

Postage: *Foreign $3.50; PUAS and Canada $2.50*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

CHEMICAL REVIEWS

This pre-eminent review journal was founded in 1924. It presents authoritative, critical reviews and comprehensive summaries of recent research in theoretical chemistry—up to 30 in six annual issues.

The reviews give a systematic presentation of the facts, theories, ideas, and mechanisms which have developed over a period of time. One condition of publication is that no review of the subject has appeared anywhere in the literature in the previous ten to twelve years.

Each review includes a complete bibliography, which provides a ready means of obtaining a large number of authoritative references.

Editor: *Dr. Ralph L. Shriner*

1 year: *ACS members* *$10.00*
All others *20.00*

Postage: *Foreign $1.50; PUAS and Canada $1.00*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

The bimonthly JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, now in its twelfth year, has developed into a major organ of scientific information in the rapidly growing fields of agricultural and food processing chemistry.

AG AND FOOD concentrates on the chemicals and the chemistry (or chemical engineering) involved in the farm production of food, feed, and fiber crops, in the processing of these harvested crops, and in the metabolism of these foods and feeds by man and animal.

Editor: *Philip K. Bates*

1 year: *ACS members* $10.00
All others 20.00

Postage: *Foreign $1.50; PUAS and Canada $1.00*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

JOURNAL OF CHEMICAL AND ENGINEERING DATA

Started in 1959, this quarterly journal represents a new departure in technical publishing. Its articles are confined almost entirely to the presentation of data, with no requirement for novel experimentation or theoretical interpretation: data alone versus ideas and theories.

Data on the behavior and properties of materials, in themselves or as they react to given conditions, are presented in two major categories: (1) data obtained through known concepts or by known methods, or extensions of such data—e.g., phase equilibria, molecular transport, thermodynamics; and (2) data listing physical properties as ends in themselves, or as aids to other studies and calculations.

JC&ED's quarterly volume each year presents some 175-200 articles for immediate use and future reference.

Editor: *Dr. Bruce H. Sage*

1 year: *ACS members* ..... *$ 9.00*
All others *18.00*

Postage: *Foreign $1.50; PUAS and Canada $1.00*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

JOURNAL OF CHEMICAL DOCUMENTATION

This quarterly journal is the first in the field to devote itself exclusively to papers dealing with the art and science of documentation. It offers up to 20 articles per issue, plus News and Notes, and Book Reviews.

Papers cover information services, searching methods, technical writing, machine translation, nomenclature, patents, indexing, mechanical information processing, abstracting, classification systems.

JCD is useful to research chemists, librarians, and information specialists and those in the field of scientific communication.

Editor: *Dr. Herman Skolnik*

1 year: *ACS members* ..... $ 7.00
All others 10.00

Postage: *Foreign $1.50; PUAS and Canada $1.00*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Publications of the
AMERICAN CHEMICAL SOCIETY
1155 Sixteenth Street, N.W.
Washington, D. C. 20036

Please enter my 1965 subscription to:

☐ JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (semimonthly)

☐ THE JOURNAL OF ORGANIC CHEMISTRY (monthly)

☐ THE JOURNAL OF PHYSICAL CHEMISTRY (monthly)

☐ BIOCHEMISTY (monthly)

☐ INORGANIC CHEMISTRY (monthly)

☐ JOURNAL OF MEDICINAL CHEMISTRY (bimonthly)

☐ ANALYTICAL CHEMISTRY (monthly)

☐ INDUSTRIAL AND ENGINEERING CHEMISTRY (monthly) with

- ☐ PROCESS DESIGN AND DEVELOPMENT (Q)
- ☐ FUNDAMENTALS (Q)
- ☐ PRODUCT RESEARCH AND DEVELOPMENT (Q)

Note: The monthly is sold only in conjunction with one or more quarterlies.

☐ JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY (bimonthly)

☐ CHEMICAL REVIEWS (bimonthly)

☐ JOURNAL OF CHEMICAL AND ENGINEERING DATA (quarterly)

☐ JOURNAL OF CHEMICAL DOCUMENTATION (quarterly)

☐ I am an ACS member and entitled to member rates.

NAME

ADDRESS

SIGNATURE DATE

See foregoing pages for member and nonmember prices. An invoice will be sent to you for the proper amount, including postage.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Road traffic flow: some theories and their applications

Digitized by Arya Samaj Foundation Chennai and eGangotri

A. J. Miller

The increasing congestion on the roads of the more developed countries has led to attempts to investigate traffic flow scientifically. A number of models of the flow have been established and have led to results that can be applied in practice. One application has shown that imposing an artificial restriction on the flow of vehicles entering a tunnel actually increases the flow.

The problem of ensuring that the flow of vehicles along a road is as high as possible is complicated in towns by, for example, conflicting traffic streams and pedestrians. Even on the open road, when a particular vehicle is unimpeded by such factors, the flow may be below the maximum possible. It is important to study why this occurs.

Traffic flow that is unimpeded, in the above sense, can be classified under one of three headings:

1. Very light traffic in which vehicles travel independently of one another.
2. Moderately heavy traffic in which traffic flows in a series of bunches, and in which vehicles, other than the slowest, travel alternately freely and constrained.
3. Very heavy traffic in which the speed of every vehicle is largely determined by that of the vehicle ahead.

There are no distinct boundaries between these three classes, though quite different models have been built up for each, and so far there has been little success in attempts to build one unifying model.

For very light traffic flows, probability models for the positions and speeds of vehicles are obviously necessary. Such models have been applied, for instance, to the deduction of the distribution of different sizes of gap in the flow, and hence to the determination of the distribution of waiting times for pedestrians or vehicles waiting for gaps so that they can cross the traffic stream.

There have been two basically different approaches to the study of moderately heavy traffic flows. One is to apply queuing theory; the other uses an analogy with the kinetic behaviour of gases. The first approach has produced some useful understanding of the relative influence on the sizes of bunches and on vehicle speeds of the flow of traffic, the ease of overtaking, and the amount of opposing traffic. The analogy with the kinetic behaviour of gases has not so far been very fruitful. An initial difficulty in making the analogy was that, in two or more dimensions, particles travelling at the same speed can collide; in one dimension they cannot. In one dimension it is relative speeds that are relevant and absolute speeds enter only when one attempts to determine actual rates of flow.

This article is largely devoted to the consideration of very heavy, 'nose-to-tail' traffic flows. Here there have been broadly three types of approach. The first uses entirely empirical methods, the second uses an analogy with the flow of fluids in channels, and the third uses models based on the response of the following vehicle in any pair to the relative motion of the vehicle ahead.

The analogy with the flow of fluids has now largely been rejected, not because it is too macroscopic, but because of the breakdown of one of its principal assumptions. This is the assumption that there is a relationship between flow and concentration during changes of speed which is the same whether the vehicles are accelerating or decelerating. For small changes of speed this assumption appears to be fairly realistic, but it breaks down when vehicles are forced to stop or almost stop. The reason for the breakdown appears to be the difference in urgency to the driver between acceleration and deceleration. Also, the act of changing from decelerating to accelerating is time-consuming, so that vehicles which were following one another at intervals of, say, 2 seconds before being forced to decelerate may be able to accelerate again afterwards only at intervals of, say, $2\frac{1}{2}$ seconds. This means that bottlenecks in the traffic stream that result from deceleration waves can lead to losses in capacity (figure 1). This feature is not present in the usual analogy with fluid flows.

Perhaps the most interesting developments in traffic flow theory have been in car-following models. These models attempt to explain the behaviour of heavy traffic by studying the 'microscopic' behaviour of traffic, rather than the 'macroscopic' behaviour used in fluid flow analogies. In this article the consequences of one of the earlier car-following models will be discussed, together with improvements intended to rectify its limitations. The car-following models developed and tested so far have been almost entirely deterministic, but have led to a number of useful discoveries. The development of a stochastic model should make it possible to establish the frequency of deceleration waves and the distribution of their magnitudes. This could lead to a valuable insight into the problem of the control of freeways and similar facilities. At present there is very little theory, and the control is not very successful.

The flow-concentration curve

As the speeds of the vehicles increase, the distance that a driver chooses to keep between himself and the vehicle in front increases more rapidly. The result is that there is a speed at which the flow of vehicles past a point is at its maximum.

The earliest model that was used in an attempt at deducing the speed at which the flow is maximized assumed that each vehicle follows the one in front, in the same lane, at a distance such that, if the first vehicle stops instantaneously, the next is just able to stop without a collision. If the reaction-time of the driver and vehicle is Δ seconds and the vehicle decelerates at a steady rate a ft/sec^2, the distance required to stop from speed v ft/sec is

A. J. Miller, *M.Sc., Ph.D.*

Was born in England in 1936 and studied at Manchester University. He graduated in Mathematical Statistics and then did research into delays caused by bunching in rural traffic. After lecturing for three years in the Department of Transportation at Birmingham University, he emigrated in 1964 to Australia. He now works at the Institute of Highway and Traffic Research in Sydney. His two principal fields of research have been traffic flow theory and the application of statistical methods in traffic engineering.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

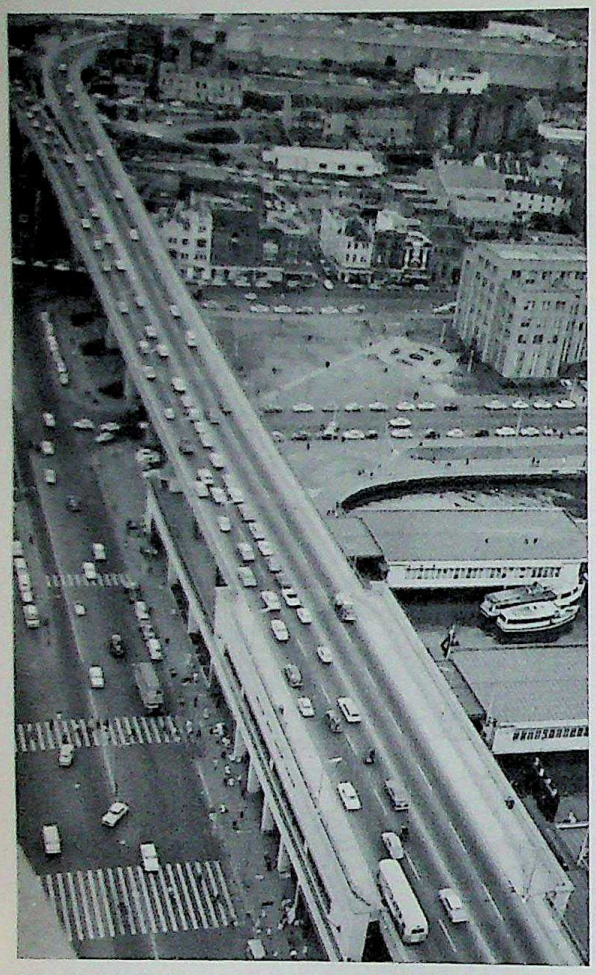


Figure 1 A deceleration wave in lane 2 in traffic on the Cahill Expressway in Sydney travelling towards the Harbour Bridge. The deceleration wave travels back from the bridge toll booths.

$$v\Delta + v^2/2a \text{ ft} \qquad \ldots\ldots(1)$$

Hence in fully saturated flows we should expect vehicles to pass a point at intervals of time (headways)

$$\Delta + (v/2a) + (b/v) \text{ sec} \qquad \ldots\ldots(2)$$

where b is the average length in feet of the vehicles. The speed to give the maximum flow or minimum headways is then

$$\sqrt{(2ab)} \text{ ft/sec} \qquad \ldots\ldots(3)$$

In the British Highway Code, a reaction time of $\frac{2}{3}$ sec and a deceleration of $22\frac{1}{2}$ ft/sec^2 have been assumed in calculating stopping distances on dry road surfaces. Using these values, one finds that the maximum flow of 1980 vehicles per lane per hour will occur, for vehicles with an average length of 15 feet, when they travel at 17 miles per hour. In practice, the observed maximum flows of private cars in unimpeded flow have ranged from about 1300 vehicles per lane per hour at 18–19 miles per hour in New York tunnels (where long reaction times can be expected because of the reduced visibility) to about 2300 vehicles per lane per hour at over 30 miles per hour on freeways in the United States and at signal-controlled intersections in Australia. This crude model thus suffers from two principal faults: it cannot explain the high flows that have frequently been observed at high speeds, and it does not explain how the average speed is determined in practice and how it is related to the flow.

The flow-concentration curve introduced by J. G. Wardrop [1] is a useful way of describing the experimentally determined relationship between speed, flow, and concentration (figure 2). If an average of k vehicles per mile of road travel at an average speed $\bar{v}$ miles per hour, the flow q, in vehicles per hour, past a point is

$$q = k\bar{v} \qquad \ldots\ldots(4)$$

The average speed used here is the so-called space-mean speed. This is obtained by averaging the speeds of vehicles over a length of road at an instant of time; it can be measured from a pair of aerial photographs taken a short interval of time apart. This is not the usual method of measuring vehicle speeds and gives a value that is usually lower than that of the time-mean speed—determined from measurements at a fixed point over a period of time. Wardrop has given a simple formula for converting one average speed to the other when vehicles maintain constant, though different, speeds over the length of road for which the concentration has been measured. The difference between the two kinds of average speed is in practice usually about 3–4 per cent.

As the concentration of vehicles increases, the speed decreases; the result is that the relationship between flow and concentration is of the kind illustrated in figure 2. The corresponding relationship between speed and flow is illustrated in figure 3. In figure 2, the gradient of the line from the origin to any point is the average speed corresponding to that point on the curve: the gradient of the line OX is the average speed when the flow is so light that no vehicle is impeded by any other. An important feature of the two figures is that, in general, the same flow is possible at two different speeds. Broadly speaking, the right-hand side of the flow-concentration curve and the lower half of the speed-flow curve represent nose-to-tail traffic conditions; the other part represents conditions under which at least some of the vehicles are unimpeded by the next vehicle ahead, and where there may be large gaps in the traffic stream. Most of the available evidence suggests that the break between the two conditions occurs slightly to the left of the apex of the flow-concentration curve. To the left of the break, although more traffic could use the section of road being considered, either no more wants to use the road or there is an upstream bottleneck that prevents more from using it. To the right of the break in conditions, as much traffic as is able is using the road and the flow is determined only by the speed at which it is able to travel.

A serious drawback to the practical use of the flow-concentration curve is that to obtain points on the curve it is necessary to take averages; if there is any variation in speed from vehicle to vehicle, a different curve is obtained for each different averaging period, length of road, or number of vehicles.

A way of avoiding these averaging difficulties is to use in calculations the distances or times—the headways—between consecutive vehicles. Two types of headway must then be distinguished—those in which the second vehicle in each pair is impeded by the vehicle ahead and those in which it is not. The left-hand side of the flow-concentration curve represents conditions in which a mixture of the two types of headway exists. D. J. Buckley

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

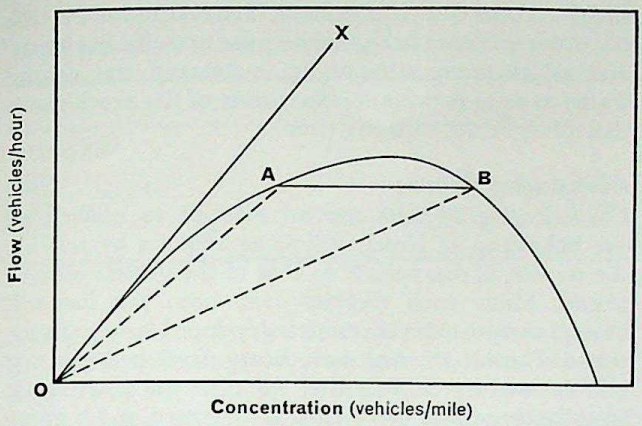


Figure 2 A flow-concentration curve.

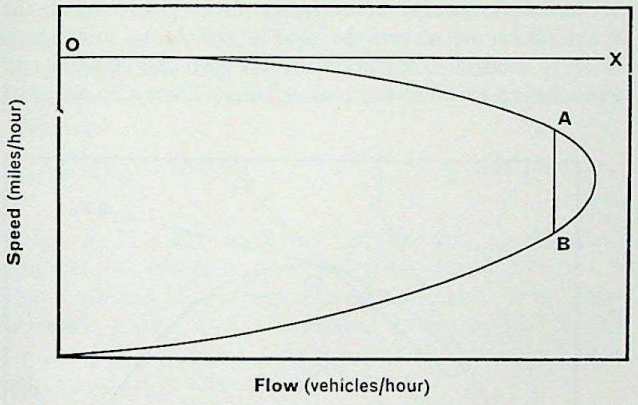


Figure 3 A speed-flow curve.

[2] has carried out a thorough analysis of the distributions of the two kinds of headway and has given a method for separating them. Less sophisticated methods have also been given by the author [3] and by A. Daou [4]. Daou has shown that, for vehicles impeded by the one ahead, the distances apart at which different drivers choose to travel at any given speed vary considerably. (They have approximately a log-normal distribution—that is, the logarithms of their values have a Gaussian distribution.)

Figure 4 shows the geometric mean distances (front axle to front axle) between consecutive vehicles travelling in the same direction on a two-lane rural road in Sweden. Only those pairs of vehicles were used for which the relative speed was within the range ± 4 km/hr, and for which the headway was not greater than 8 seconds. The straight line was fitted to the logarithms of the separation distances by the method of least squares. The parallel lines are limits that enclose about 95 per cent of the observations. The fitted regression line, the equation relating D_g, the geometric mean distance in metres between vehicles, and v, the speed in km/hr, is

$$\ln D_g = 1{\cdot}441 + 0{\cdot}034v \qquad \ldots.(5)$$

If one applies the usual statistical calculations, using an estimated standard deviation of the log-distances of 0·61, one finds that the arithmetic mean distance

$$D_a = 5{\cdot}09e^{0{\cdot}034v} \text{ metres} \qquad \ldots.(6)$$

Notice that this gives an average separation distance of 5·09 metres (a little more than one car length) for stationary vehicles. This is a remarkably good and slightly fortuitous extrapolation, as most of the observations were in the speed range 45–75 km/hr. The reciprocal of D_a is the concentration. By multiplying by the speed, the speed-flow table below was obtained.

Speed v (km/hr)	10	20	30	40	50	60
Flow q (vehicles/hr)	1400	1990	2120	2010	1780	1520

The speed at which the maximum flow can be obtained is the reciprocal of the gradient in (5); in this case it is about 29 km/hr.

The flow-concentration curve fitted by this empirical method is of the form

$$q = -ck \cdot \ln (k/k_j) \qquad \ldots.(7)$$

where k_j is the 'jam-concentration', that is, the concentration when the vehicles are stationary, and c is the speed for maximum flow, known as the characteristic speed. This flow-concentration curve has been fitted to various sets of data by H. Greenberg [5], D. C. Gazis, R. Herman, and R. B. Potts [6], and L. C. Edie [7], but in each case for speeds lower than in the example given here. There have been at least two theoretical derivations of the form (7), one of which will be given later.

The Lighthill-Whitham theory

M. J. Lighthill and G. B. Whitham [8] produced a theory of traffic flow on 'crowded' roads that was an analogy with river flow. The theory is based upon the flow-concentration curve and assumes that statistical fluctuations may be ignored when traffic flow is examined on a sufficiently macroscopic scale. The theory attempts to explain the speed at which waves are propagated in a traffic stream, the formation of 'shock-waves', and flow through bottlenecks.

If q and k are the flow and concentration respectively on a length of road, then for an observer moving at speed v on a parallel path, the rate of flow past him is

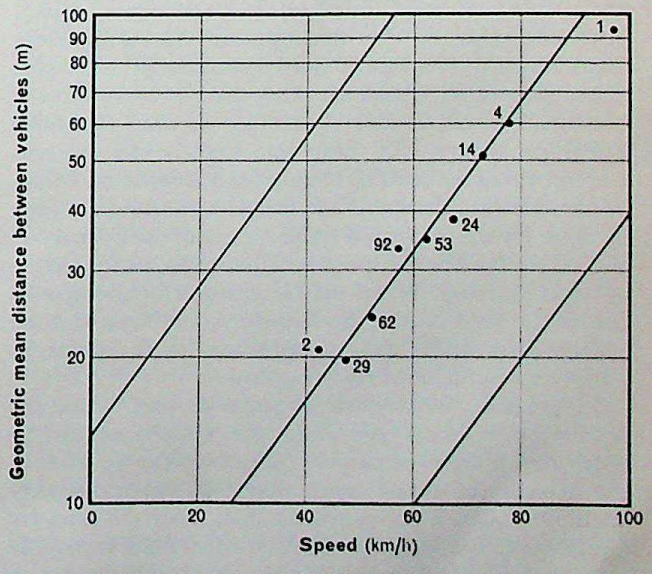


Figure 4 Geometric means of distances between front axles of consecutive vehicles plotted against speed. The means are of all the distances for each particular 5 km/hr speed class. The numbers of observations in each class are shown beside each plotted point.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

$(q-kv)$. Now consider two observers travelling a fixed distance apart and at such a speed that the average number of vehicles between them remains constant. Let us suppose that there are acceleration and deceleration waves in the traffic stream, but that these are such that the same mathematical relationship between flow and concentration holds in all cases. Suppose (q, k) and $(q+\delta q, k+\delta k)$ are the flows and concentrations respectively at the two positions of the observers at any particular time. For the flow past the two observers to be the same we must have

$$q-kv=(q+\delta q)-(k+\delta k)v \qquad \ldots.(8)$$

That is

$$v=\delta q/\delta k \qquad \ldots.(9)$$

If we assume that flow and concentration change continuously rather than abruptly, this result means that regions of constant concentration, 'waves', travel at a speed equal to the gradient of the tangent to the flow-concentration curve (figure 2) at the relevant concentration. Thus, for the left-hand side of the flow-concentration curve, waves travel forwards; for the right-hand side, they travel backwards. Since the tangent at any point has a gradient which is less than that of the line to the origin, waves always travel backwards relative to the average speed of the traffic stream.

When discontinuities occur, as for instance when a bunch of vehicles is released from a traffic signal, the arguments used to derive (9) are still applicable (if they were in the first case); the speed of the edge of the discontinuity or 'shock-wave' is given by the gradient of the chord joining the flow-concentration points for each side of the shock-wave (figure 5). The front of the shock-wave in this case is the front of the bunch released by the signals. The shock-wave speed is approximately the average of the wave speeds before and after the discontinuity, and is exactly the average if the q-k curve is parabolic.

Lighthill and Whitham applied their theory to the flow of vehicles through a junction and through a bottleneck. This latter application would be extremely useful, but unfortunately the assumptions can completely break down in this case. Figure 6 shows a q-k curve for either side of a bottleneck, with the q-k curve for the bottleneck itself inside. According to the Lighthill-Whitham theory, the flow into the bottleneck can increase up to the level A, the bottleneck capacity. In the bottleneck itself the speed and concentration should then be those for the same flow on the inner of the q-k curves, and on the far side the speed and flow should be the same as upon entering. When the incoming flow attempts to exceed the level of A, a shock-wave should form and the approaching traffic flow jump across to the point B, which represents slow, crawling flow.

In practice, what often happens is that when the bottleneck becomes saturated the conditions in the bottleneck jump to some point D rather than C. That is, the capacity of a bottleneck may fall, sometimes substantially, when it becomes saturated. Once the capacity has fallen below the rate of inflow of vehicles it may be hours before free flow is restored. This is well known to the inhabitants of Sydney. At points on rural roads many miles out of Sydney it is possible to observe a flow in one direction of about 1400 vehicles/hour on a two-lane road until the shock-wave forms, when the flow drops to about 600 vehicles/hour. The realization that the fall occurred came as a great surprise to traffic engineers, and led to many attempts to understand and control traffic so as to prevent the formation of the shock-waves that precede the capacity drop.

Car-following theories

Car-following theories are an attempt to understand the behaviour of closely following vehicles by relating the motion of one vehicle to that of the vehicle directly ahead. Many such theories have been put forward, though in most cases the models developed have not been tested. Possibly the first such theory developed was that put forward by A. Reuschel [9]. The most significant contributions have come from R. Herman and a group of associates at the General Motors Research Laboratories [6, 10, 11].

Herman's group assumed in their model that the acceleration of a vehicle closely following another is linearly related to the distance between the vehicles and the relative speed of the two vehicles. They also assumed

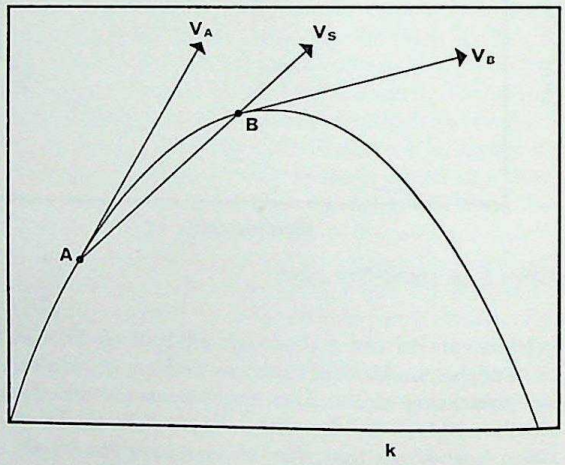


Figure 5 Use of the q-k curve to find shock-wave speeds. V_A=speed of waves ahead of the discontinuity, V_B=speed of waves behind, V_S=speed of the shock-wave.

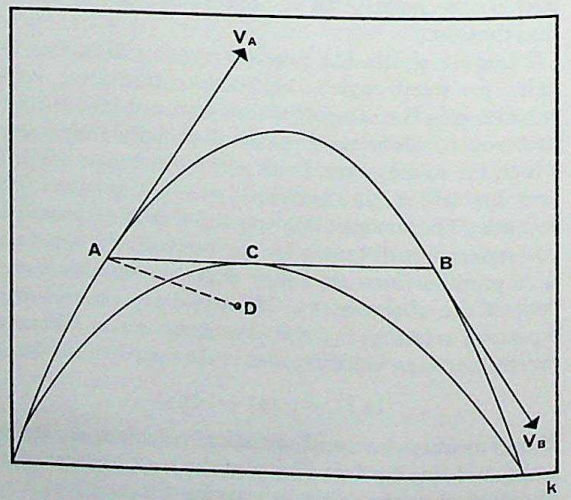


Figure 6 V_A=speed of waves approaching a bottleneck just before it is saturated, V_B=speed of wave after the 'crawl' has developed. The curve through C is the q-k curve in the bottleneck.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Table I

Values of sensitivity λ and reaction time Δ

Driver:	1	2	3	4	5	6	7	8
Δ (sec)	1·4	1·0	1·5	1·5	1·7	1·1	2·2	2·0
λ (sec^{-1})	0·74	0·44	0·34	0·32	0·38	0·17	0·32	0·23
$\frac{1}{\lambda}\left(\frac{1}{\lambda}-2\Delta\right)$	−2·0	+0·6	−0·2	+0·4	−2·0	+22	−4·0	+1·5

a time lag due to the reaction time of the second driver and vehicle. Experiments were then conducted on a test track using two vehicles with a wire wound round a spring-loaded drum connecting them. The rotation of the drum gave a continuous record of the distance between the vehicles. Eight different drivers took part in the test runs, which lasted between 20 and 30 minutes each. The driver of the leading vehicle varied his speed irregularly, between 10 and 80 miles per hour.

In the analysis of the results for each driver, the model used was

$$\ddot{x}_2(t) = \mu[x_1(t-\Delta) - x_2(t-\Delta)] + \lambda[\dot{x}_1(t-\Delta) - \dot{x}_2(t-\Delta)] \quad \ldots.(10)$$

where x, $\dot{x}$, $\ddot{x}$ are positions, speeds, and accelerations respectively, either at time t or time $(t-\Delta)$, where Δ is the combined driver-vehicle reaction time. (The parameters μ, λ, and Δ were estimated by the method of least squares.) It was found that the first term had very little effect and so it was rejected, leaving

$$\ddot{x}_2(t) = \lambda[\dot{x}_1(t-\Delta) - \dot{x}_2(t-\Delta)] \quad \ldots.(11)$$

Thus the acceleration of the second car is proportional to a value involving the speed of each car, and its total reaction time. The constant λ is called the 'sensitivity' of the driver of the second car. Table 1 gives the values of λ and Δ obtained for each of the eight drivers [11].

This car-following law, as derived for two cars, can be extended to a line of following cars, and it can be shown that the condition for a wave caused by a fluctuation in the speed of the first vehicle to be damped down as it travels back is

$$\sum_i \frac{1}{\lambda_i}\left(\frac{1}{\lambda_i} - 2\Delta_i\right) > 0 \quad \ldots.(12)$$

where λ_i, Δ_i are the sensitivity and reaction time for the ith vehicle. These terms are shown in table 1, which shows that four of the drivers tend to amplify waves and the other four damp them down. The calculations thus confirm the common-sense view that the ideal driver is one who reacts quickly (Δ short), but not violently (λ small), to any change in the speed of the vehicle ahead.

A further result that can be deduced from (11) is that the average speed of deceleration or acceleration waves in cars per unit time is equal to the harmonic mean of the values of λ. Using the values in table 1, we find that it takes an average of 3·2 seconds for a wave to travel from one vehicle to the next. This means that waves travel forwards when the average headway is less than 3·2 seconds (flow = 1125 vehicles/hr), and backwards when the average headway is greater than 3·2 seconds.

If these results are representative of driving in practice, it means that in dense traffic, conditions are just on the verge of instability and that the chance occurrence of several consecutive vehicles whose drivers have long reaction times could bring about a breakdown in flow. In most cases in practice, though, it is not reasonable to apply equation (11) to each consecutive vehicle in a line, as drivers are usually able to see deceleration waves well ahead of them and to take action in plenty of time.

An important feature of car-following models is the emphasis given to relative speeds and changes of speed rather than to absolute speeds. Drivers do not leave sufficiently large gaps ahead of themselves to enable them to avoid the vehicle ahead if it stops suddenly; instead they judge the amount by which the vehicle ahead may change its speed. Where variations in speed are small, for instance at intersections with separate lanes for turning vehicles, and with no parked vehicles or bus stops, vehicles follow one another much more closely than usual. It is in such cases that variations in speed, because they are unexpected, can lead to serious shock-waves and sometimes to chain collisions.

Closer examination of the General Motors data led to the conclusion that the sensitivity parameter depends on separation distance, and the model was revised [6, 10] to

$$\ddot{x}_2(t) = \lambda_0 \cdot \frac{\dot{x}_1(t-\Delta) - x_2(t-\Delta)}{x_1(t-\Delta) - x_2(t-\Delta)} \quad \ldots.(13)$$

Integration then gives

$$\dot{x}_2(t) = \lambda_0 \ln [x_1(t-\Delta) - x_2(t-\Delta)] - \text{constant} \quad \ldots.(14)$$

When there are no speed fluctuations, so that Δ can be left out, this gives the flow-concentration curve (7); λ_0 will then equal the characteristic speed. The value obtained from the General Motors experiments was 27·4 m.p.h. The detailed analysis of the propagation of waves for this model does not appear to have been undertaken. It would probably be found that small deceleration waves would be damped out, whereas a sharp deceleration by one vehicle would be amplified by successive vehicles until vehicles are brought completely to a halt. The behaviour of this model in this respect is analogous to that of epidemics [12]. When the number of persons infected is small, the probability of an increase in the number infected is also small, so that there is a good chance of eliminating the disease. Once the number infected exceeds a critical level, the chances of avoiding a full epidemic are small.

The control of tunnels and freeways to prevent shock-waves

On many freeways and tunnels in the United States, and in a few cases in other countries, average speeds drop to 10 m.p.h. or less during the morning and evening peak periods. Since it is known that, at other times, these roads handle more traffic at higher speeds, large sums of

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

money are being spent to prevent the formation of the shock-waves that lead to these low speeds. Among the best known of the control projects are those of the Holland tunnel in New York and of the Eisenhower Expressway in Chicago. More than $1 000 000 has been spent so far on the second of these, and even more has been spent on other similar projects.

In the control of the Holland tunnel it was recognized that there was a permanent source of deceleration waves. This was at the point where vehicles start to climb to leave the tunnel. In the peak periods, whenever a group of vehicles travelling at closer than average headways reached this point, the deceleration wave was amplified; within seconds the traffic in that lane would be at a standstill as far back as the tunnel entrance. This situation was successfully prevented [13] by inserting gaps in the entering traffic. Whenever 22 vehicles entered the tunnel in one lane in less than a minute, the traffic was stopped for the remainder of the minute. (The particular rate was chosen empirically.) Thus whenever conditions were right for the deceleration wave to be amplified, a gap was deliberately inserted to absorb the wave. This increased the peak hour flow by about 6 per cent, reduced tunnel breakdowns by 25 per cent, and reduced the cost of ventilation of the tunnel by 60 per cent. Further improvements have now been made by automatically varying numbers of vehicles entering according to the speed in any bottleneck.

In the case of the Eisenhower Expressway, it is traffic entering the expressway that has to be controlled so as to prevent the formation of shock-waves. The control logic in this case is far less fully developed, though two useful findings have been reported [14]. The first of these is a simple method of estimating concentrations. If all the vehicles passing a point have a length l and speed v, the time taken for the whole vehicle to pass a point is l/v. If q vehicles/hour pass a point, the proportion of the time during which part of a vehicle is passing the point is $ql/\bar{v}$, where $\bar{v}$ is the harmonic mean speed of the vehicles; Wardrop [1] showed this is the same as the space-mean speed. That is, the proportion of the time during which vehicles are passing is equal to the product of the concentration and the length of the vehicles. This result is still valid if vehicle lengths vary, but needs a correction if long vehicles, say, are found to travel at slower than average speeds.

The second interesting finding is that in wet weather drivers travel further apart and deceleration waves are never amplified; it is not necessary to control the expressway in wet weather. This suggests that the cheapest method of expressway control may be to spray the road with water during peak periods!

Conclusion

The theory of traffic flow has advanced very rapidly in the last few years, particularly since the first symposium on the subject was held in Detroit in 1959. In this article it has been possible to refer to only a small selection of topics; readers wishing to learn more are recommended particularly to investigate references [1, 10, 15, 16].

Acknowledgments

I acknowledge with thanks the assistance given by the Australian Mutual Provident Society in photographing traffic on the Cahill Expressway, and by Austin Morgan of the Traffic Engineering School, University of New South Wales, in the taking and processing of the photograph.

References

[1] Wardrop, J. G. *Proc. Instn civ. Engrs*, 3, 158, 1952.
[2] Buckley, D. J. *Proc. Aust. Rd Res. Bd*, 1, pt. 1, 153, 1963.
[3] Miller, A. J. *Jl R. statist. Soc.*, Series B, 23, 64, 1961.
[4] Daou, A. 'On flow within platoons'. Research report (unpublished) of the Port of New York Authority. 1964.
[5] Greenberg, H. *Ops. Res.*, 7, 79, 1959.
[6] Gazis, D. C., Herman, R., and Potts, R. B. *Ibid.*, 7, 499, 1959.
[7] Edie, L. C. *Ibid.*, 9, 66, 1961.
[8] Lighthill, M. J. and Whitham, G. B. *Proc. R. Soc.* A, 229, 317, 1955.
[9] Reuschel, A. *Öst. Ing. Arch.*, 4, 193, 1950.
[10] Herman, R. and Potts, R. B. In 'Theory of traffic flow', p. 120. Elsevier, Amsterdam. 1961.
[11] Chandler, R. E., Herman, R., and Montroll, E. W. *Ops. Res.*, 6, 165, 1958.
[12] Bartlett, M. S. 'Stochastic population models'. Methuen, London. 1960.
[13] Greenberg, H. and Daou, A. *Ops. Res.*, 8, 524, 1960.
[14] Athol, P. 'The interdependence of certain operational characteristics within a moving traffic stream'. Report No. 11, Eisenhower Expressway Surveillance Project, Chicago, 1963.
[15] Haight, F. A. 'Mathematical theories of traffic flow'. Academic Press, New York. 1963.
[16] Cleveland, D. E. and Capelle, D. G. In 'An introduction to traffic flow theory', p. 49. U.S. Highway Res. Board, Special report 79. 1964.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

The search for a variable-speed induction motor

Digitized by Arya Samaj Foundation Chennai and eGangotri

F. C. Williams and J. F. Eastham

Induction motors normally run at speeds that are close to integral fractions of the frequency of the electrical supply, while variable-speed motors need external connections to the rotating parts. This article describes the methods that were used in attempts to make a variable-speed induction motor, and the motors, some of which were economically valuable, that arose from the work.

Technological research may be divided into two broad classes, inventive and developmental. Inventive research proceeds in a series of discontinuous jumps that result from the introduction of some new concept, while developmental research makes progress by the steady application of improved materials and better design. Inventive research is the more exciting of the two, but developmental research can have quite dramatic results over a reasonable period of time. For example, the contemporary motor car is basically the same as its counterpart of 40 years ago, but it is vastly cheaper in real terms and much more reliable. However, this article is concerned with inventive rather than developmental research. The work to be described is the output of a team whose individual members have each contributed much, but whose effect on each other has contributed more.

This article gives the broad history of a search for an improved variable-speed electric motor. Because the problems were challenging and the prospects of ultimate success not high, the project was extremely suitable for university study. The work as described had an accidental beginning; it followed a tortuous path to the point it has now attained; and it has reached no end. There are no conclusions that can be drawn, except perhaps that, even though progress in projects of this type is very rarely made by a direct path, all the steps taken, including those in the wrong direction, seem to be essential to the thought processes of the individual concerned.

Scientifically and educationally, the effort has been stimulating, and many new machines have been devised, but these machines, when matched against the existing systems, have not presented sufficient advantages to win ready acceptance from industry. Although each device was scientifically better than existing motors, in that it had some demonstrable advantage, in nearly every case the advantage would be purchased at too high a price. Any one of them would have been 'better than nothing', but none of them was judged 'better than what we have' in economic terms. However, there were, as we shall see, other gains from the research.

Available machines

Most driven industrial machinery uses three-phase squirrel-cage induction motors. This machine, which is shown in figure 1, is unique in that it requires no connections to the moving part. It is therefore robust, comparatively inexpensive, and requires little maintenance. However, a standard induction motor can be designed to operate only at speeds slightly below certain fixed speeds, which are integral fractions of the frequency of the mains supply. The motor is thus essentially a fixed-speed machine.

If variable-speed working is required, electrical connections to the rotor are necessary. These connections may be provided by brushes and either slip-rings or a commutator. In both cases, power flows through rubbing contacts, and this gives rise to the possibility of trouble due to sparking and mechanical wear. Intensive development over the years has permitted the manufacture of highly reliable slip-rings and commutators, but regular maintenance is still required; in addition, brushes cannot be tolerated in some special circumstances. It thus remains highly desirable to devise brushless variable-speed drives. The squirrel-cage induction motor is brushless; the problem is to understand the restrictions on its speeds, and avoid them if possible.

Basic principle and limitation of induction motors

The alternating currents that flow in the stationary conductors of an induction motor produce a moving magnetic field. The most familiar analogy of this mechanism is the generation of waves on the sea. These waves sweep across the sea, but the water that generates them does not. This, however, does not prevent a skilled surf-rider from using the wave motion to propel him towards the beach. If attention is confined to a narrow strip of the surface of the water, it is evident that its level oscillates. Consideration of a succession of such strips shows that each strip oscillates at the same frequency and amplitude, but that the motions differ progressively in relative timing, so that a phase difference exists between the

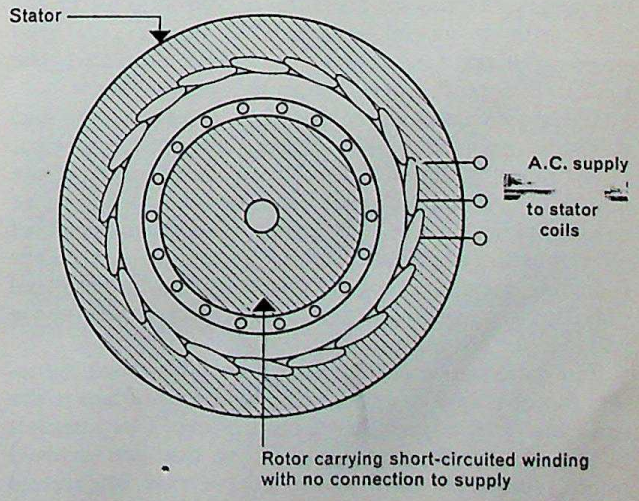


Figure 1. Basic squirrel-cage induction motor.

F. C. Williams, *C.B.E., D.Sc., M.I.E.E., F.R.S.*
Was born in 1911 and educated at Manchester University and at Magdalen College, Oxford. Since 1946 he has been Professor of Electrical Engineering at the University of Manchester.

J. F. Eastham, *M.Sc., Ph.D.*
Was born in 1933 and educated at Manchester University, where he now holds a post as lecturer in the Department of Electrical Engineering.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

oscillations of successive strips. The wavelength of the travelling wave is determined by the distance separating strips that oscillate in the same time phase, and the wave speed is given by the frequency of oscillation multiplied by the wavelength.

The stator of a linear induction motor forms an electrical version of the wave mechanism. Each slot of the motor shown in figure 2 contains currents that oscillate at the supply frequency, but again there is a progressive change of relative time phase, indicated by the progressive change in shade from wire to wire. Thus a travelling wave of current results. The moving current distribution produces a travelling magnetic field which will cause a lateral force on a sheet of conducting material. The size of the force is a function of the velocity of the travelling field relative to the sheet. Thus if the sheet is allowed to accelerate (in the absence of retarding forces due to friction or windage) it reaches a limiting speed equal to the speed of the field. The sheet cannot travel faster than the wave, in the same way that a surf-rider cannot approach the beach faster than the wave propelling him; however, unlike the surf-rider, the sheet can travel slower than the wave and still experience a driving force.

A conventional induction motor is formed by rolling up a section of a linear motor to produce a cylindrical stator as shown in figure 3. A section containing a whole number of wavelengths must be used in order to produce the smoothing rotating field which is essential for the proper working of the machine. In machine terminology, a half-wavelength is usually termed one pole pitch, and if 16 poles (8 wavelengths) are rolled into a cylindrical form, no discontinuity is formed, whereas rolling up 15 poles results in a discontinuity that is stationary in space. The necessity of using a whole number of wavelengths produces the restriction on the number of field speeds that can be produced economically by induction motors. If one wavelength is used around the machine periphery, the field performs one revolution in one cycle of the supply. If two wavelengths are used, the field speed is halved, to produce one revolution in two supply cycles, and so on. Thus the rotational field speeds are given by $60f/$(number of wavelengths) r.p.m., where f is the supply frequency in cycles per second. The number of poles, P, on the machine is twice the number of wavelengths, and the expression may be rewritten as $120f/P$. This means that, using a supply frequency of 50 c/s, rotational speeds of 3000, 1500, 1000, . . . can be produced; the values are $6000/P$, where P must be an even integer.

The rotor cannot rotate at exactly the field speed and still produce torque. There must be relative motion. However, it is a fundamental scientific property of the machine that the efficiency cannot exceed the rotor speed divided by the field speed, and rotor speeds of 98 per cent of the field speed are commonly used. Thus induction motors with good efficiency can be produced only for a particular set of speeds, and speeds above 3000 r.p.m. are not possible on a 50 c/s supply.

The importance of designing a variable-speed induction motor that does not use electrical connections to the rotor has been appreciated for some time. Our attempts at Manchester to solve the problems that are involved might, therefore, have arisen from a cold intellectual approach; in fact, our interest in the programme was purely accidental.

Origins of the work

Some experiments were being made in our department using linear motors for propelling loom shuttles to and fro. We realized that the stators of such linear motors could drive a disk, as illustrated in figure 4, and that the rotational speed of the disk could be varied by altering the distance R. The problem of speed variation without brushes is obviously solved by this machine from a purely scientific point of view. However, it is also obvious that the problem is not solved from a technological point of view, if only because the area of disk operated on by the field is small.

Here the matter would have ended if the experiment had not exposed a very interesting situation, illustrated by figure 4. The conductor is not travelling in the same direction as the field at the ends of the stator of linear motor, and it was realized that the behaviour of a conductor in these circumstances was not known, nor was it immediately obvious. Some of us predicted that the conductor would travel at a speed that approached the component of field speed in the direction of motion of the conductor. In this case, the conductor would travel more slowly than the field and

$$V_c = V_f \cos\theta \qquad \ldots.(1)$$

where θ is the angle between the field and conductor directions, V_c the conductor velocity, and V_f the field velocity. Others predicted that the component of conductor speed in the direction of motion of the field must approach the field speed, that is that the conductor would travel at a greater speed than the field speed, and

$$V_c = \frac{V_f}{\cos\theta} \qquad \ldots.(2)$$

This issue was resolved by experiment. Figure 5 illustrates the apparatus. The handle in the picture adjusts the angle θ, and the question of whether equation (1) or equation (2) is correct can be decided by direct observation of an increased or reduced speed as θ is altered from zero. An increase of speed was observed, and immediately the fallacies of the arguments leading to equation (1) were apparent to all, as was the inescapable logic of the arguments leading to equation (2).

Many years after this principle had been established, it was noticed that surf-riders at Laguna Beach in California used this method to remain poised on the wave slope. They were, incidentally, increasing their speed through the water in their direction of travel by approaching the beach at an angle. The surf-riders provide a useful example of the angled use of wave motion; figure 6 illustrates the situation. If the surf-rider is propelled by the wave front shown initially in the figure at a distance x from the beach, and remains on the same wave front as he approaches the beach at an angle θ to the direction of motion of the waves, then, in the time the wave takes to travel the distance x, the rider must travel a distance $x/\cos\theta$ and must therefore be travelling faster in his own direction than the waves in theirs.

The 'angled field method' suggested a new form of brushless variable-speed drive. Furthermore, it was at least scientifically sound, because it is clear that as θ is increased, the torque on the disk must be reduced (being zero when $\theta = 90°$). Had the speed also decreased with increasing θ, the power output and efficiency would also have been reduced. However, since the speed increased,

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

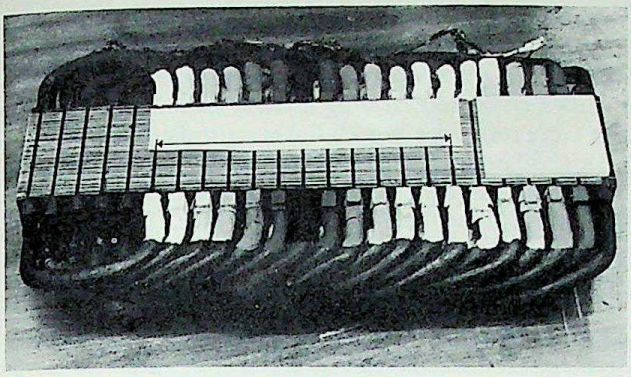


Figure 2 A linear induction motor. (The arrows show one wavelength.)

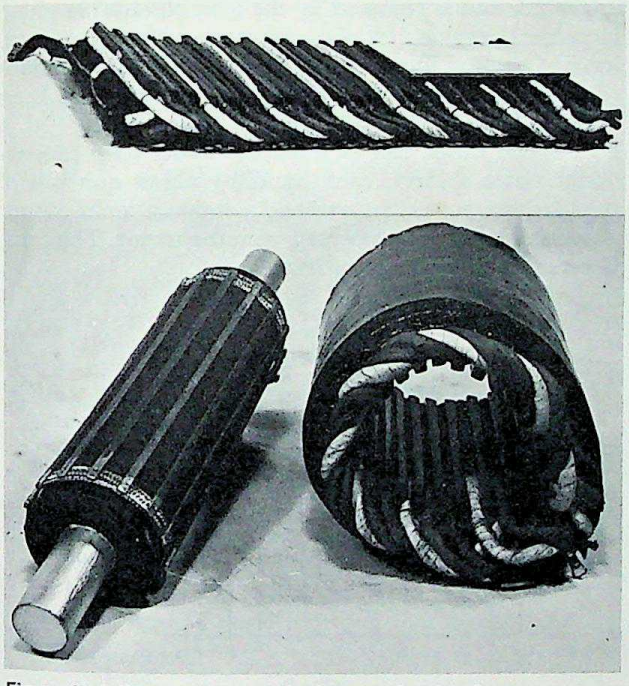


Figure 3 A linear motor can be 'wrapped up' to form a cylindrical rotary machine.

these reductions were not inevitable, and some further investigation was indicated, even though the disk machine was itself a technological failure.

Development of 'angled field' motors

Almost all practical induction motors use rotors in the form of cylindrical barrels; this configuration makes the optimum use of the copper and iron employed. However, if the field structure is to be 'angled', the rotor clearly must be spherical, if a small constant distance is to be maintained between the stator and the rotor. Several machines using part-spherical rotor barrels (figure 7) were built, and they operated satisfactorily [2, 3]. The results showed that the machines were very nearly acceptable, but the cost of the construction of part-spheres discouraged manufacture.

It was clear that if a method could be found of inclining the field electrically, rather than mechanically, this would be much more attractive, particularly if it permitted a return to cylindrical rotors. A great deal of time and effort was devoted to the problem of electrically inclined fields, and several unsuccessful machines were constructed. It is not worth while to describe these experiments, because it should have been obvious that we were going in the wrong direction. However, the experiments did contain the germ of a much easier solution. A mechanically angled field is shown in plan in figure 8. The travelling field is shown as a stationary pattern of 'north' and 'south' poles, appropriate to a particular instant in time. If attention is confined to the narrow strip contained between the dotted lines, it is apparent that, as the angle θ increases, adjacent north and south poles are spaced by a greater distance; that is, the pole pitch increases. Thus, since velocity is proportional to pole pitch, conducting material constrained to move at an angle θ to the travelling wave moves faster than the wave.

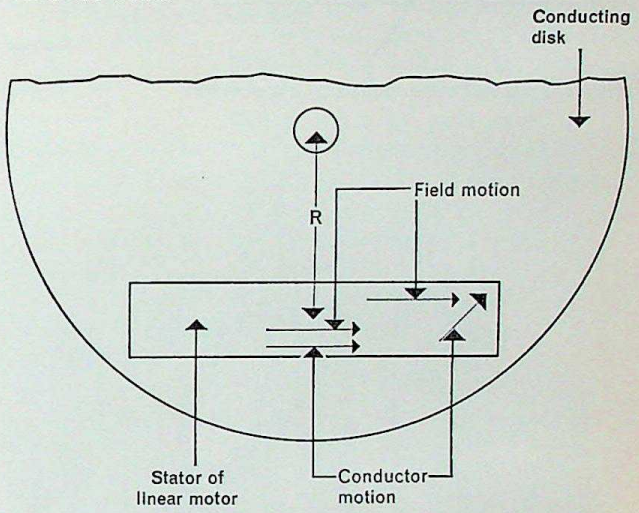


Figure 4 The action of the disk motor.

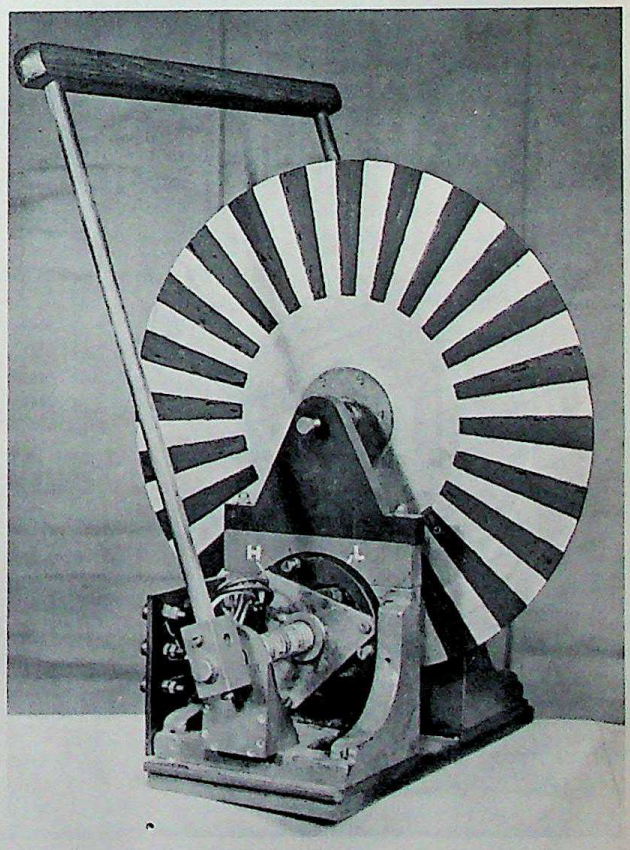


Figure 5 Experimental 'angled field' disk motor.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

In the linear motor, the wavelength is the distance between the slots containing conductors carrying the same phase of current. The wavelength may therefore be varied either by altering the separation between the slots, which is impracticable, or, conversely, by changing the phase of currents supplied to a set of conductors fixed in space. This mechanism is illustrated by figure 9, which shows a set of slots forming a linear motor. The phase of the current flowing in each slot is controlled by a separate phase shifter—a common electrical device. The distance along the block at which the starting phase recurs depends on θ, the phase increment per slot. If, for example, $\theta = 60°$, slot 6 would contain the same phase of current as slot 0, and one wavelength would be contained in $6D$, where D is the distance between slots. In general, the pole pitch is $180D/\theta$, and the wave velocity may be controlled, without mechanical movement of the stator block, by varying θ.

At this point, the angled field concept has disappeared, and is replaced by the idea of variable phase increment per slot. It is of course intolerably expensive to use one phase shifter per slot, but two modified methods of supplying the variable-phase slot currents have been devised. In one solution, known as 'phase mixing' [4], a 2 : 1 speed range can be obtained using four conventional phase shifters, each handling about one-fifth of the machine power. In a second solution a multi-output phase shifter is built integrally with the motor. The combination is known as the logmotor [5].

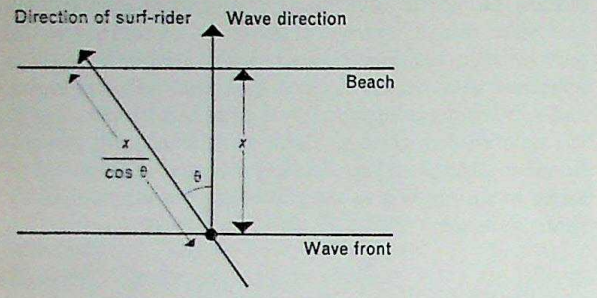


Figure 6 Use of wave motion by a surf rider.

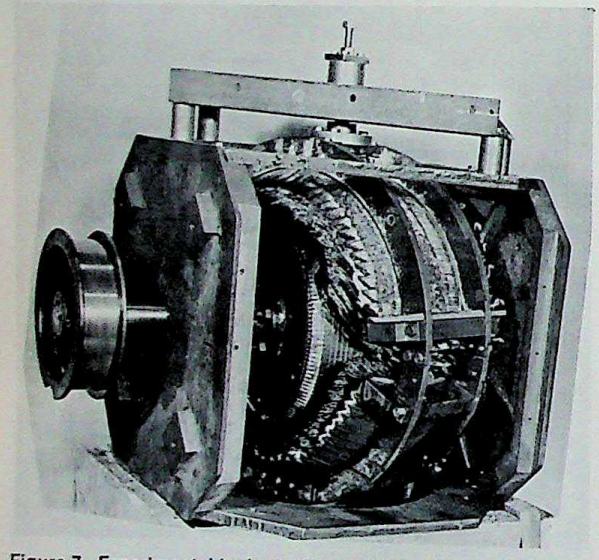


Figure 7 Experimental 'spherical motor' using 'angled field' principle.

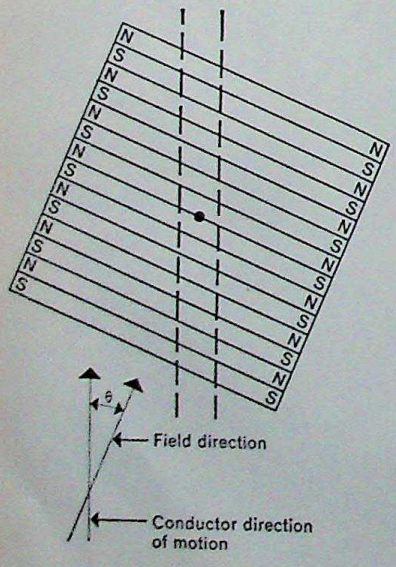


Figure 8 The derivation of the 'pole-stretching' technique from the 'angled field' principle.

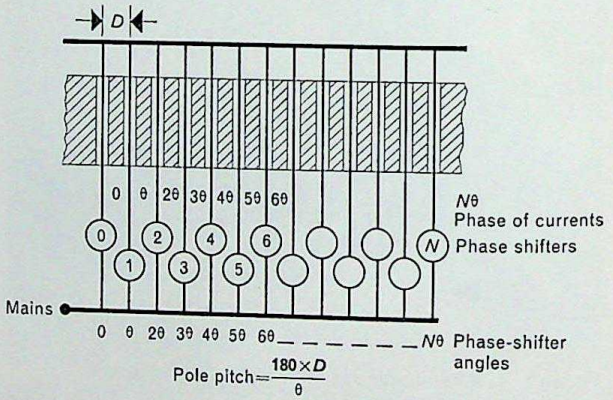

D
0 θ 2θ 3θ 4θ 5θ 6θ
Nθ
Phase of currents
0 1 2 3 4 5 6 N
Phase shifters
Mains
0 θ 2θ 3θ 4θ 5θ 6θ — — — — — Nθ Phase-shifter angles
Pole pitch = 180×D / θ

Figure 9 Basic 'pole stretch' motor.

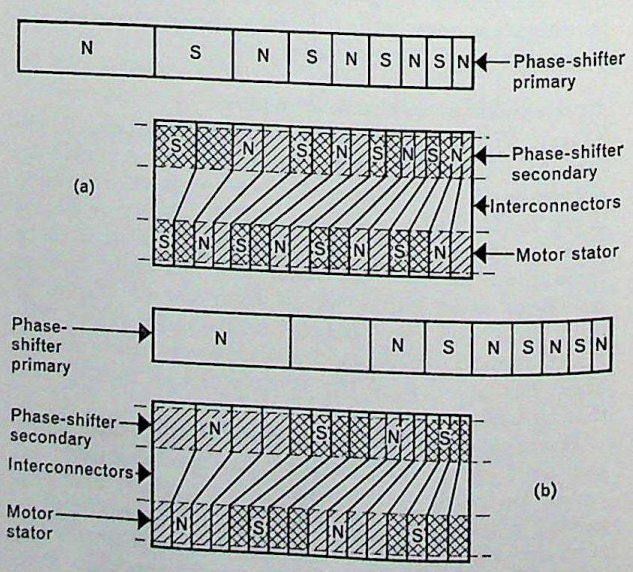


Figure 10 The principle of the logmotor.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

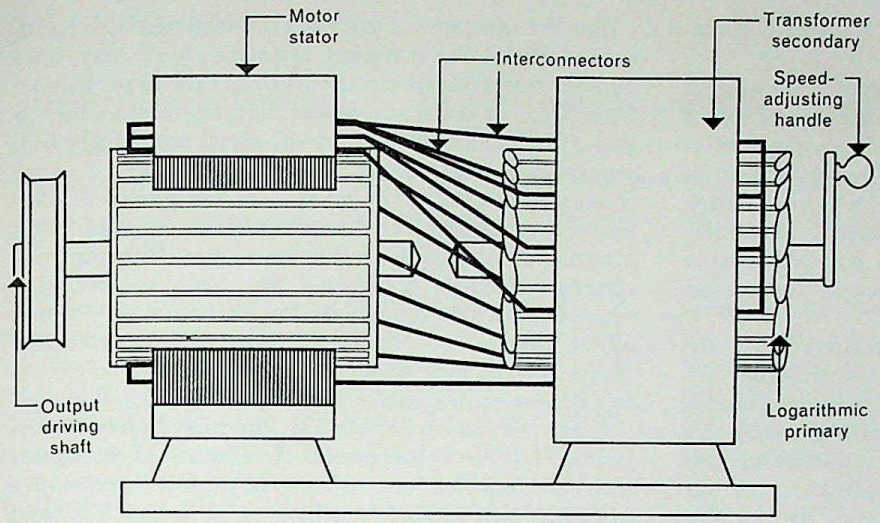


Figure 11 The logmotor, a 'pole stretch' machine with built-in phase shifter.

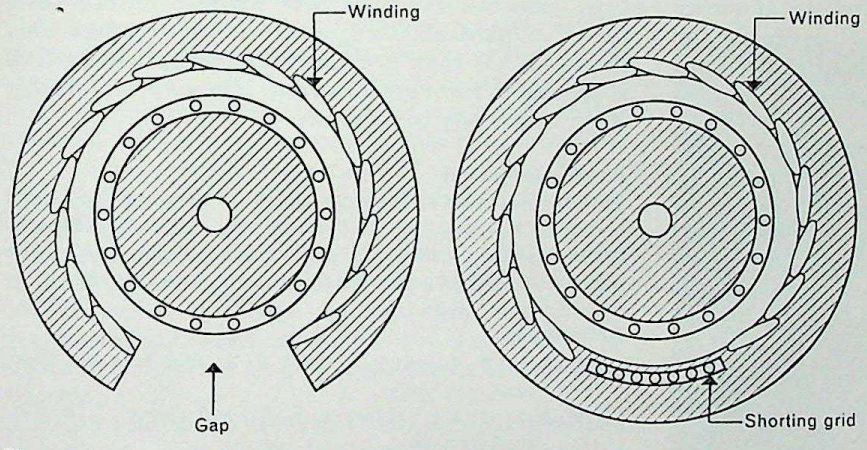


Figure 12 The production of a 'break' in the field pattern by omitting part of the stator iron, or by means of a short-circuited section on the stator.

The principle of one form of logmotor is illustrated by figure 10. The rotor of the phase shifter contains a winding producing a travelling field. The pole lengths produced by the winding follow a logarithmic law. The stator of the phase shifter carries a set of conductors in slots which are logarithmically spaced, and these conductors are connected directly to the evenly spaced slots of the induction motor. If the rotor winding on the phase shifter is in the position shown in figure 10a, currents that produce eight poles on the induction motor stator are induced in the interconnectors. If the motor winding is moved to the position shown in figure 10b, four poles are produced on the motor stator. This phase shifter uses the slide-rule principle, and hence intermediate motor pole pitch lengths are possible. A drawing of the complete machine is shown in figure 11.

Both the logmotor and the phase-mixer motor were very nearly successful; this time the main difficulty was that a large proportion of the power traversed two devices, the phase shifter and the motor proper, and each device contributed its quota of loss.

It is important to emphasize at this point that the spherical motor, logmotor, and phase-mixer motors would all have been 'better than nothing'; but they were not sufficiently successful to replace the traditional alternatives, such as d.c. machines or a.c. commutator motors.

Mathematical approach

The work which has been described so far was made very laborious by the need to construct and test many experimental models because the analysis of the machines involved was largely undeveloped. The main difficulties in the mathematics stem from the requirement, in variable pole pitch machines, to keep the end and the beginning of the excitation separate. This separation may be achieved either by a break in the stator iron or by a grid of short-circuited conductors (see figure 12). The need for such a break is shown by figure 13, which is a plot of speed against control position or pole pitch. If the machine begins with a pole pitch appropriate to say 11·8 poles around the machine periphery, it is found that the machine speed corresponds almost exactly with 12 poles, that is 500 r.p.m. on a 50 c/s supply. Reducing the number of poles from this value to, say, 10·5 poles does not materially affect the speed, but if the process is continued, a point is reached at which the speed suddenly jumps to the speed appropriate to 10 poles—600 r.p.m. This behaviour continues over the whole range of operation—the machine speed jumps discontinuously from one preferred synchronous speed to the next.

The reason for this behaviour can be understood by considering a particular element of the rotor as it passes through the excitation. It will carry a particular amount of magnetic flux, and if this is inappropriate to the state of the next part of the excitation, there will be a force on the rotor that slows or

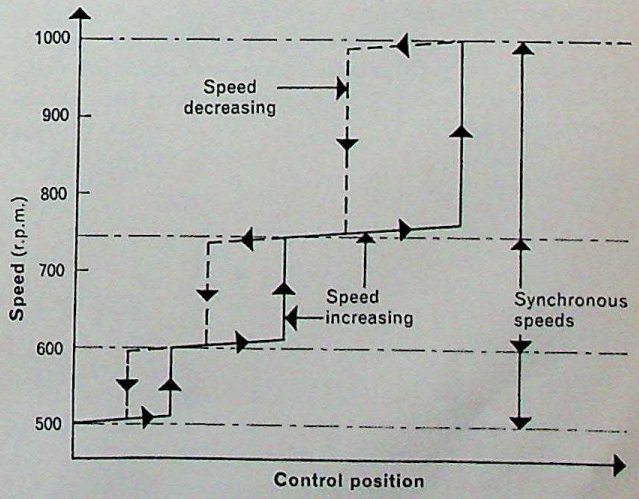


Figure 13 Machine speed versus control position for machine without a stator 'break', showing discontinuous speed change with hysteresis. ↑, Speed increasing; ↓, speed decreasing; – – –, synchronous speeds.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

accelerates it to a synchronous speed. If there is a discontinuity, this problem is avoided.

Thus the break in the excitation is essential for smooth speed variation, and under these conditions a portion of the rotor is sensibly unexcited before it enters the influence of the winding; the excitation then builds up as the portion of the rotor passes under the excited part, only to fall to zero again under the influence of the break. The rotor behaviour is therefore of a transient nature even at fixed rotor speeds, and predicting the performance of such machines is difficult.

The mathematical problems associated with the machines have, however, been solved numerically with the aid of a digital computer [6], and it is now possible to 'try' the effects of different physical arrangements on a computer, rather than by laboriously constructing new machines. Regrettably enough, the results show that the machines are not quite as advantageous as was first hoped. They also show that in favourable circumstances very good machines can be constructed; unfortunately these favourable circumstances are of rather infrequent occurrence. Thus the original design for the motor has not proved successful. Nevertheless, there are a number of valuable by-products of the work.

By-products

It has just been explained that the speed jumps discontinuously from one synchronous speed to the next, if the machine has no stator break. When the control is set so that an exact even number of poles is produced, the machine performance is extremely good. A set, rather than a continuous series, of good speeds can therefore be obtained using the phase-mixer type of machine. In certain circumstances, the phase shifters used can be replaced by switches that simulate the effects of the controller at the preferred positions. The machines produced by this technique fall into a general class of machines in which a single winding is used to provide multi-speed operation. These machines are usually called pole-change machines. This by-product has been energetically pursued [7, 8] and it is now possible to design two-speed motors which are either smaller or more efficient than alternative designs using two windings. They are undoubtedly scientific and technological successes. They are also economic successes, but it remains to be seen whether industry will find them sufficiently attractive to justify abandoning their established methods.

Further extension of this work is concerned with multi-speed electric transmission systems which may have applications to diesel-electric traction or ship propulsion. Diesel-electric traction schemes normally involve the use of a d.c. generator driven by the diesel motor. The output from this generator is used to supply d.c. drive motors connected to the wheels. In the proposed alternative a.c. scheme, the d.c. generator is replaced by an alternator that supplies induction motors. By using pole-change windings, a scheme has been evolved that requires switching only at the low excitation power level of the alternator to provide a large series of induction motor speeds. The system therefore provides an economical close-ratio gearbox without using commutators.

From our own point of view, the most important by-product has been educational. An element of excitement has been injected into what was rapidly becoming a fossilized part of our teaching, and a much clearer understanding of the conventional machine has been achieved. The impact on undergraduate courses has been immense. We have been led into further work, using, in particular, silicon controlled rectifiers—thyristors—in the rotor circuits of brushless machines. This is proving to be of great interest; it is, however, another story, which may be told later.

Acknowledgment

This article is based on the Bakerian Lecture delivered to the Royal Society by Professor F. C. Williams in May 1964 and published in full in *Proceedings of the Royal Society, A*, 283, 1, 1965. The Society's approval of this further use of the material is much appreciated.

References

[1] Williams, F. C. and Laithwaite, E. R. *Proc. Instn elect. Engrs*, 102A, 203, 1955.

[2] Williams, F. C., Laithwaite, E. R., and Piggott, L. S. *Ibid.*, 104A, 102, 1957.

[3] Williams, F. C., Laithwaite, E. R., and Eastham, J. F. *Ibid.*, 106A, 471, 1959.

[4] Williams, F. C., Laithwaite, E. R., Eastham, J. F., and Farrer, W. *Ibid.*, 108A, 100, 1961.

[5] Williams, F. C., Laithwaite, E. R., Eastham, J. F., and Piggott, L. S. *Ibid.*, 108A, 91, 1961.

[6] Tipping, D. 'The Analysis of some Special Purpose Electrical Machines'. Ph.D. Thesis. University of Manchester. June 1964.

[7] Eastham, J. F. and Laithwaite, E. R. *Proc. Instn elect. Engrs*, 109A, 397, 1962.

[8] Williams, F. C., Eastham, J. F., and Piggott, L. S. *Ibid.*, 111A, 80, 1964.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Acetabularia

Digitized by Arya Samaj Foundation Chennai and eGangotri

J. L. A. Brachet

Acetabularia is a large unicellular alga that continues to develop for some months after removal of its nucleus. In addition, some parts of the cell can multiply in the absence of genes. It is therefore a valuable organism for studying the different mechanisms of inheritance and the interplay of the nucleus and cytoplasm. This article discusses the results of experiments with fragments of the alga.

A swimmer who goes to the Mediterranean at the beginning of summer will see that many of the rocks are covered with green algae; they consist of thin stalks topped by an umbrella-shaped cap (figure 1). This is *Acetabularia mediterranea*, the largest known unicellular organism. It is common on all of the Mediterranean coasts, and when it is mature, in June and July, it can easily be collected in handfuls. Other species—particularly *Acetabularia crenulata*—and different but closely related algae, of the genus *Acicularia*, are found in the subtropical and tropical seas.

As figure 1 shows, the mature plant consists of three parts. The rhizoids are root-like structures that attach the plant to the rocks. These are joined to the cap, whose shape is characteristic of the species, by a stalk that is traversed by a central vacuole. J. Hämmerling has shown [2, 3] that the length of the stalk and the size of the cap are affected by the intensity of light to which the alga is exposed; intense light favours the development of the cap at the expense of the stalk. This effect is easily seen in naturally occurring algae. Those that are found on rocks near the surface have large caps, and stalks only about a centimetre long, whereas I have found *Acetabularia* with stalks ten centimetres long on an amphora at a depth of 20 metres.

Figure 2 shows the life cycle of the plant, as described by Hämmerling [1, 2]. During most of its life the plant is unicellular, with the nucleus in one of the rhizoids. Once the cap has attained its maximum size, the nucleus forms a number of daughter nuclei by successive divisions, and these travel up the stalk to the cap. There they are enveloped, together with some of the surrounding cytoplasm, by a solid membrane, and form cysts that are released when the cap degenerates. The nuclei divide, and the amount of cytoplasm increases, until the cysts become mobile gametes. These immediately fuse in pairs to form diploid zygotes that quickly attach themselves to rocks. The stalk starts to grow and forms a number of sterile verticils that are eventually replaced by the cap. This reproductive cycle is the one usually followed by *Acetabularia*, but S. Puiseux-Dao has suggested [4] that there are sometimes others.

E. Schulze in Hämmerling's laboratory [2], and F. Vanderhaeghe in the author's, have both studied the cytology of the alga, which is at its most interesting in the period that immediately precedes the formation of the caps. The nucleus develops in a most striking way. The nuclear membrane is clearly visible, and it encloses a considerable volume of nuclear fluid and a number of large, sausage-shaped nucleoli (figure 3a). If basic stains are used, the nuclei become intensely coloured; they are basophilic because they are extremely rich in RNA. On the other hand, they contain no visible chromatin and give no reaction to tests for DNA. In all probability the small quantity of DNA present in the original zygote becomes undetectable because the volume of the nucleus is so large. There is thus an extremely large nucleus containing virtually no DNA; it is not possible to detect any until after the nucleus has degenerated and the daughter nuclei have started to move up the stalk.

The cytoplasm of the rhizoids is also rich in RNA, and

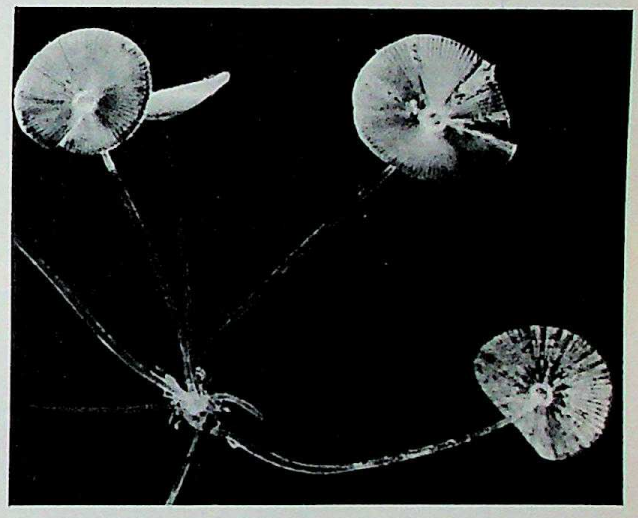


Figure 1 A clump of *Acetabularia*. The alga on the right shows cysts that have formed in the cap. (×1·5)

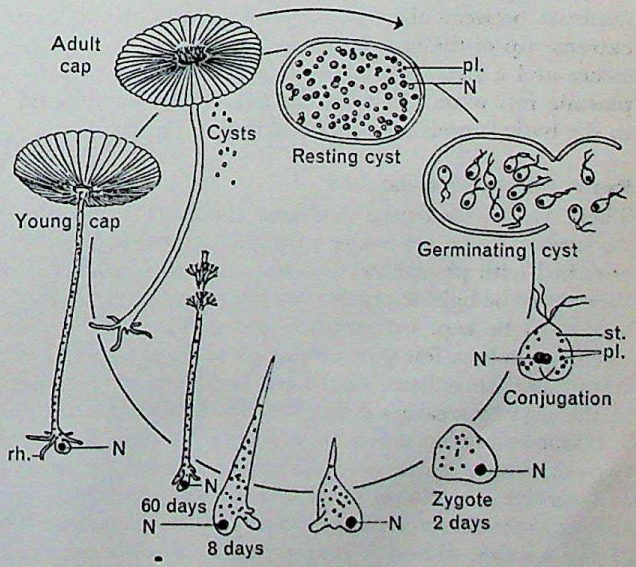
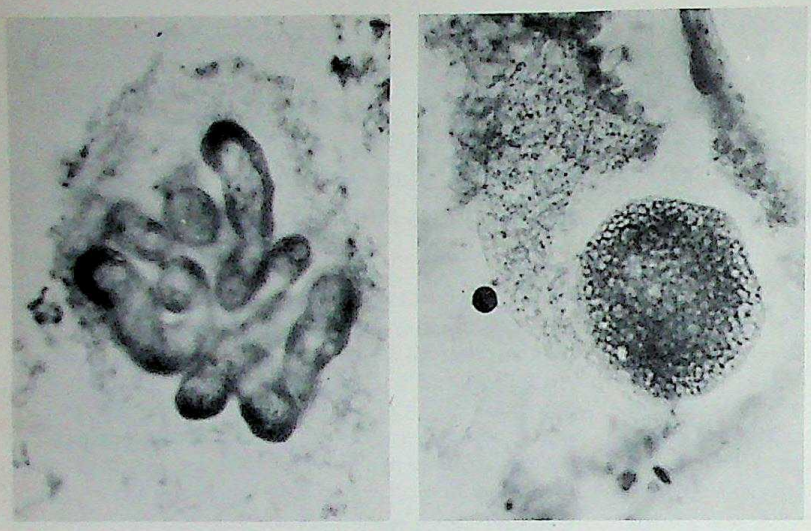


Figure 2 Life cycle of *Acetabularia*. (N = nucleus; rh. = rhizoid; pl. = plastid; st. = stigma.)

J. L. A. Brachet, *M.D.*
Was born in 1909 in Etterbeek, Belgium, and educated at the Free University of Brussels. He has been Professor of Biology there since 1938. His particular research interests are in cytology and embryology.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri



(a) (b)

Figure 3 Nucleus of *Acetabularia*. *(a)* A normal nucleus, with sausage-shaped nucleoli. *(b)* The nucleus of an alga in which the energy production in the cytoplasm has been reduced. The nucleolus is spherical and contains a vacuole. (Both × 500)

it contains, in addition, starch grains and degenerating amyloplasts; these are chloroplasts bursting with starch grains. Most of the stalk of the alga is occupied by a vacuole whose contents are acidic. The cytoplasm, which is rich in chloroplasts, is thus restricted to the periphery, and the chloroplasts themselves can be seen to undergo the continuous movement known as cyclosis. The cytoplasm is most dense at the tip of the stalk, where the cap will form, and G. Werz has shown [3] that at this point it contains both basic proteins and RNA. There is a tough cellulose membrane surrounding the entire alga.

The ultrastructure of the alga has been studied by J. C. W. Crawley [5], and in the author's laboratory by P. Van Gansen and M. Presburg. Figure 5 shows that the structure of the cytoplasm, in the upper part of the figure, where it touches the nuclear membrane is extremely complex. There is a labyrinth of membranes, which suggests that there are complex exchanges of material between the nucleus and the cytoplasm. The extreme tip of the stem contains large numbers of ribosomes and a structure of membranes forming an endoplasmic reticulum. These structures clearly correspond to the basic proteins and RNA shown by staining.

Experiments with *Acetabularia*

There are no particular problems involved in growing *Acetabularia*. The sea water in which it grows must be enriched with phosphate, nitrates, and soil extracts [6]; there must be light at regular intervals; and the temperature must be kept between 20° and 22°C. In addition, one must take a few precautions to avoid the spread of infections. The culture starts from cysts that are induced in the alga by treating it briefly with distilled water.

Hämmerling has shown [1, 2] that if the alga is cut in two—a simple operation—the part without a nucleus can survive for several months and can regenerate. It will produce a cap with the shape that is characteristic of the species, although it is generally slightly smaller than the cap on a normal alga. Figure 4 shows a group of such caps, and it will be seen that they are indistinguishable in shape from those on the normal algae shown in figure 1. Experiments such as these demonstrate a fact of fundamental importance. A cap can be produced with a shape that is characteristic of the species, and thus genetically determined, in circumstances such that there is no nucleus present, and therefore there are no genes. In other words, a phenotype is produced in a system that is completely devoid of genes. There must therefore be stable intermediates between the genes and the phenotype.

We shall consider the chemical nature of these intermediates later. The biological experiments [1–3] show that the morphogenetic substances that are produced by the nucleus accumulate at the tip of the stalk, and that apical fragments, although devoid of a nucleus, can always form a cap. The central portion of the stalk, which has neither apical fragments nor a nucleus, cannot regenerate.

The experiments have also shown that the morphogenetic substances that originate in the nucleus are specific in their nature. Figure 6 shows the results of grafting a nucleus-containing part from one species to a nucleus-free part from another. The effect of the nucleus will always dominate all the other influences in the end, and this dominance is even more marked if two parts containing a nucleus are grafted to one without.

It is thus clear that parts of the stalk that have no nucleus contain substances that originated in the nucleus, that are characteristic of the species, and that are essential for morphogenesis, in the sense of cap-formation. These substances accumulate at the tip of the alga. These conclusions have been confirmed by K. Zetsche's studies on the transplantation of nuclei. He was able to show clearly that the morphogenetic substances are

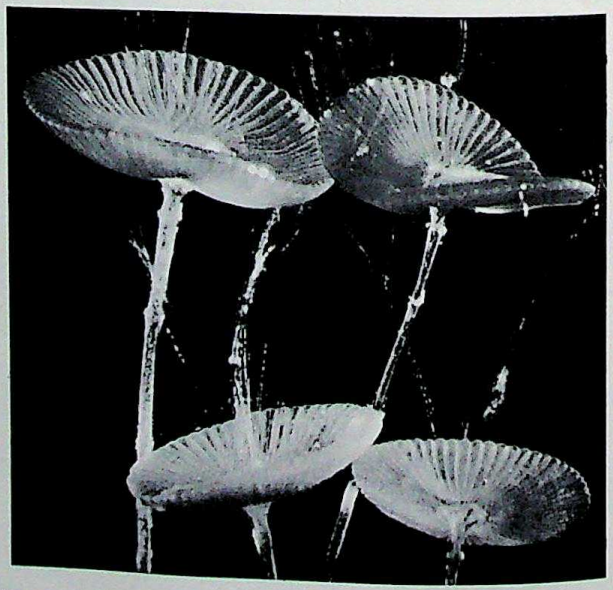


Figure 4 Caps formed from enucleated fragments of normal algae. (× 2)

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

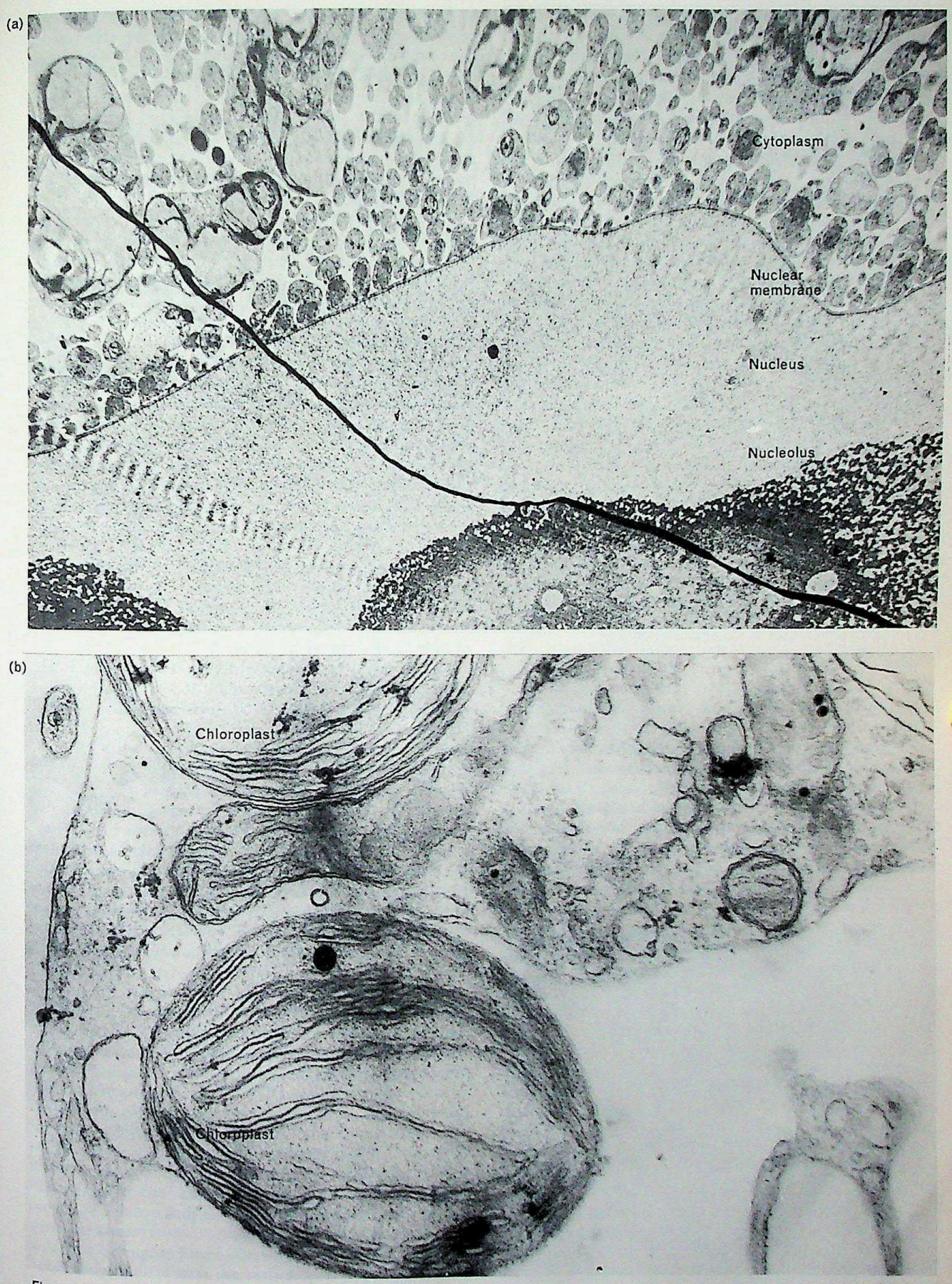


Figure 5 Ultrastructure of a normal *Acetabularia*. *(a)* The nucleus with its nucleoli can be seen at the bottom; above this is the cytoplasm near to the nucleus. (×8000) *(b)* Chloroplasts. (×42 000)

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

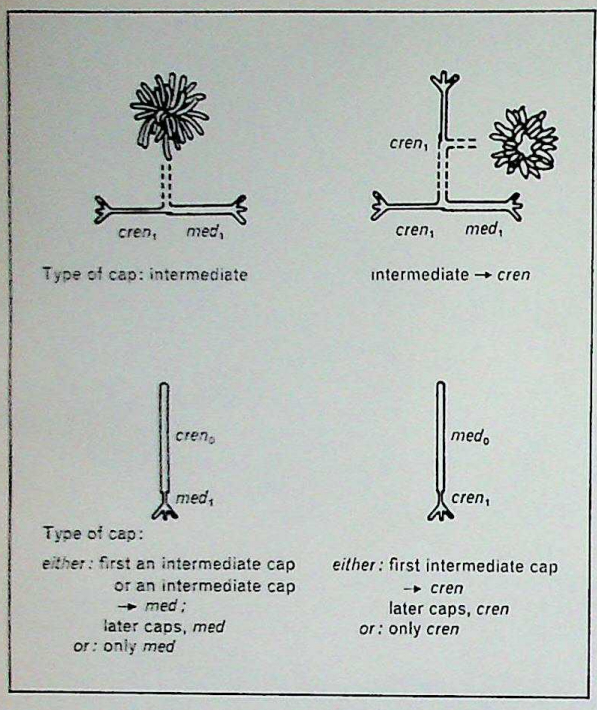


Figure 6 Schematic representation of the results of grafts between *Acetabularia mediterranea* and *A. crenulata* [2]. (*cren*$_1$, *med*$_1$ = *A. crenulata*, *A. mediterranea*, fragments each with a nucleus; *cren*$_0$ = enucleated *crenulata* fragment; intermediate cap = a cap of a type intermediate between that of each species; → *cren* = a preponderance of the characteristics of *A. crenulata*)

produced by the nucleus, and not by the surrounding cytoplasm.

The work that we have described concerns the effect of the nucleus of *Acetabularia* on the cytoplasm; but this alga also shows effects in the opposite sense, those of the cytoplasm upon the nucleus. Hämmerling has shown [2] that repeated sectioning of the stalk will stop the nucleus from entering division. Thus there are factors that are essential to nuclear division present in the cytoplasm of those algae that are about to form caps. Another effect is revealed if the alga is kept in the dark for a few weeks. This reduces the rate of energy production in the cytoplasm, and H. Stich has shown [7] that this in turn causes the nucleus to shrink. In addition, the nucleoli become spherical, form a vacuole, and diminish in RNA content. These changes in the nucleus are reversible, and we have shown [6] that they also occur if oxidative phosphorylation is prevented by the addition of dinitrophenol (figure 3b).

The work in the author's laboratories has concentrated on the biochemistry of both nucleated and enucleated fragments of *Acetabularia*; in general, the results agree with those of Hämmerling [3]. They can be summarized as follows [8–10].

1. Energy production remains normal in enucleate fragments for a period of several weeks; the rate at which oxygen is consumed and the rate of photosynthesis are also unaltered during this period. These results lead to the important conclusion that the mitochondria and the chloroplasts, the sites of these activities, are largely independent of the nucleus in their functions.

2. Enucleate fragments are capable of a net synthesis of protein for at least three weeks after the removal of the nucleus. The proteins that are made include a number of enzymes, such as aldolase, fructosidase, and phosphorylase. One group of enzymes, the phosphatases, have been studied in some detail by C. Keck, T. Spencer, and H. Harris, and by E. Triplett and A. Steens; most of these enzymes can be synthesized by enucleate fragments, and the cytoplasm is even able to control the rate of synthesis.

These observations lead to an important conclusion. It is normally held that the synthesis of protein is controlled by genes; enucleate fragments of *Acetabularia*, on the other hand, can make specific proteins—enzymes—without genes. This synthesis must be controlled by cytoplasmic factors that store all the genetic information that is needed for amino acids to be assembled into polypeptide chains. It is striking that these factors can exist in cytoplasm for at least three weeks without losing genetic information.

3. The question of whether RNA can be synthesized in enucleate fragments of *Acetabularia* has been a matter of controversy for a long while. It now seems certain that the synthesis can occur under suitable conditions; of these, light seems to be the most important. It is fragments cut from specimens of *Acetabularia* that have been kept in the dark for a few days that give the most abundant net synthesis of RNA once they are exposed to light. This synthesis was observed in the author's laboratory in 1955 [8]. It is mainly chloroplast RNA that is made, which suggests a reason for the importance of light in 'enucleate' synthesis.

M. Janowski has recently shown that transfer RNA, ribosomal RNA, and chloroplast RNA are all synthesized eight to ten days after the removal of the nucleus. However, his experiments show that chloroplast RNA is peculiar, as it becomes directly associated with DNA.

4. We have already published evidence [9, 10] which suggests that the chloroplasts of *Acetabularia* incorporate thymidine, which is a specific precursor of DNA; this has now been confirmed by our collaborator F. de Vitry. Janowski's work, quoted above, suggests that chloroplast DNA is synthesized in enucleate fragments. Lastly, E. Baltus and J. Brachet [11] and S. Izawa and A. Gibor [12] have shown that there is DNA in chloroplasts extracted from enucleate fragments of *Acetabularia*. This DNA seems to have a different composition from that of nuclear DNA.

Biochemical interpretation of these results

Any attempt to interpret these results should preferably use only the accepted ideas on the genetic control of protein synthesis (figure 7). Broadly, these are as follows. The genetic material, DNA, sends information to the cytoplasm in the form of messenger RNA (m-RNA). This corresponds exactly to the DNA, and its synthesis is effected, in the presence of DNA, by the enzyme RNA-polymerase. The action of this enzyme is specifically blocked by actinomycin, which combines vigorously with DNA. Once the various m-RNA's that are derived from the different genes have reached the cytoplasm, they attach themselves to ribosomes. These are particles with a large molecular weight that are rich in their own kind of RNA—r-RNA. The combination of ribosomes and m-RNA is called a polysome and is the actual site of

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

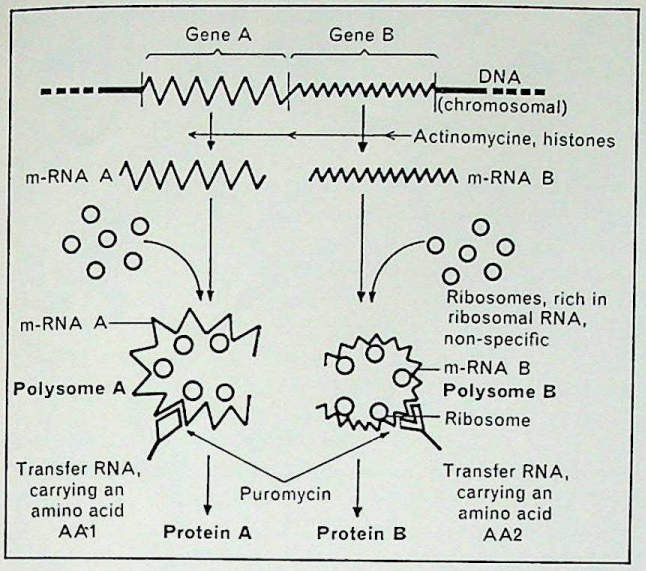


Figure 7 Schematic representation of the genetic control of protein synthesis.

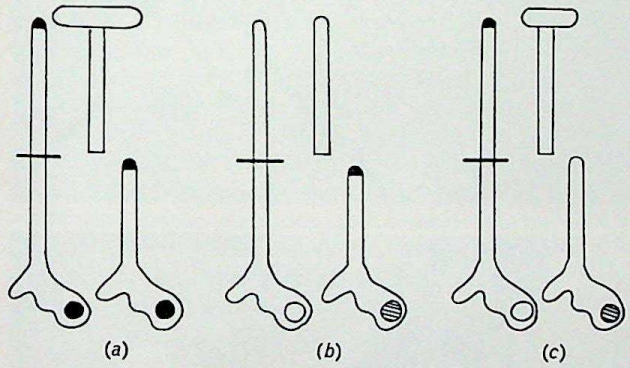


Figure 8 The distribution of messenger-RNAs. *(a)* Normal algae. *(b)* Algae treated with ribonuclease. *(c)* Algae treated with actinomycin.

protein synthesis. Transfer RNA (t-RNA) has a low molecular weight and is highly specific; it is t-RNA that brings the amino acids, in an activated state, to the polysomes. There they are arranged in a sequence, dictated by the m-RNA, so as to form the particular protein that is to be synthesized. This last stage can be specifically blocked by puromycin.

Figure 8a shows how this scheme must work in *Acetabularia*. The nucleus manufactures m-RNA's, and these pass into the cytoplasm and accumulate at the tip of the stalk: they carry the genetic information that will control the synthesis of the specific proteins that are essential for the formation of the cap. These RNA's, unlike those of bacteria, can survive for a relatively long time in enucleated cytoplasm.

This scheme is more than a mere hypothesis. M. Olszewska, working in the author's laboratory, has shown [9, 10] that RNA travels from the nucleus, where it is made, to the tip of the stalk. Confirmation of a different kind comes from the work of H. Stich and W. Plaut, who have shown [13] that ribonuclease—the enzyme that destroys RNA—blocks the regeneration of enucleate fragments permanently, but blocks that of fragments that still contain a nucleus only temporarily: this work has been repeated in the author's own laboratories. These results are easily understood in terms of the proposed scheme (figure 8b). The enzyme destroys the RNA's in the fragments, whether they have a nucleus or not; but only those with a nucleus can replace the RNA's once the ribonuclease has been removed.

We have recently studied the effect of actinomycin on the regeneration of fragments of *Acetabularia* [14]; K. Zetsche has carried out similar work independently and obtained the same results [15]. Actinomycin combines with DNA and thus prevents the synthesis of the messenger RNA's; but it has no effect on any RNA's that have already been made. It should therefore have more effect on the regeneration of fragments that still have a nucleus than on those that have not. Experiment confirms this deduction (figures 8c and 9). As figure 10 shows, actinomycin has a marked effect on the ultrastructure of both the nucleus and the chloroplasts of the treated alga.

Puromycin, which blocks the actual assembly of amino acids into proteins, prevents enucleate fragments from regenerating; this effect is only temporary for fragments with a nucleus. These results show that the formation of a cap required the synthesis of proteins.

The experiments with actinomycin have revealed one unexpected fact. Although actinomycin does not stop the initiation of the caps, it does restrict their growth. This can be seen by comparing figure 4 with figure 9. This secondary inhibition may be caused by the combination of actinomycin with chloroplast DNA. If this is what occurs, the result would be that the production of chloroplast RNA's stops; this would in turn mean that no chloroplast proteins are formed.

There is a good deal of evidence in support of this hypothesis. Experiments in the author's laboratories have shown that the chloroplasts contain DNA [11, 12], and that actinomycin combines with these chloroplasts; as a result, their fine structure becomes markedly different. This can be seen by comparing figures 5b and 10b [16]. In addition, work that has been carried out in the author's laboratory [17] and independently in Hämmerling's [18] has shown that chloroplasts from enucleate fragments of *Acetabularia* contain everything that is necessary for protein synthesis. Thus they contain

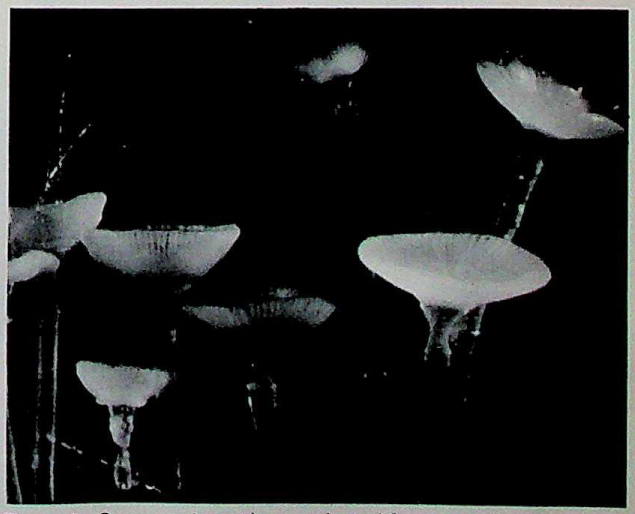


Figure 9 Caps produced by enucleated fragments in the presence of actinomycin. (×2)

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

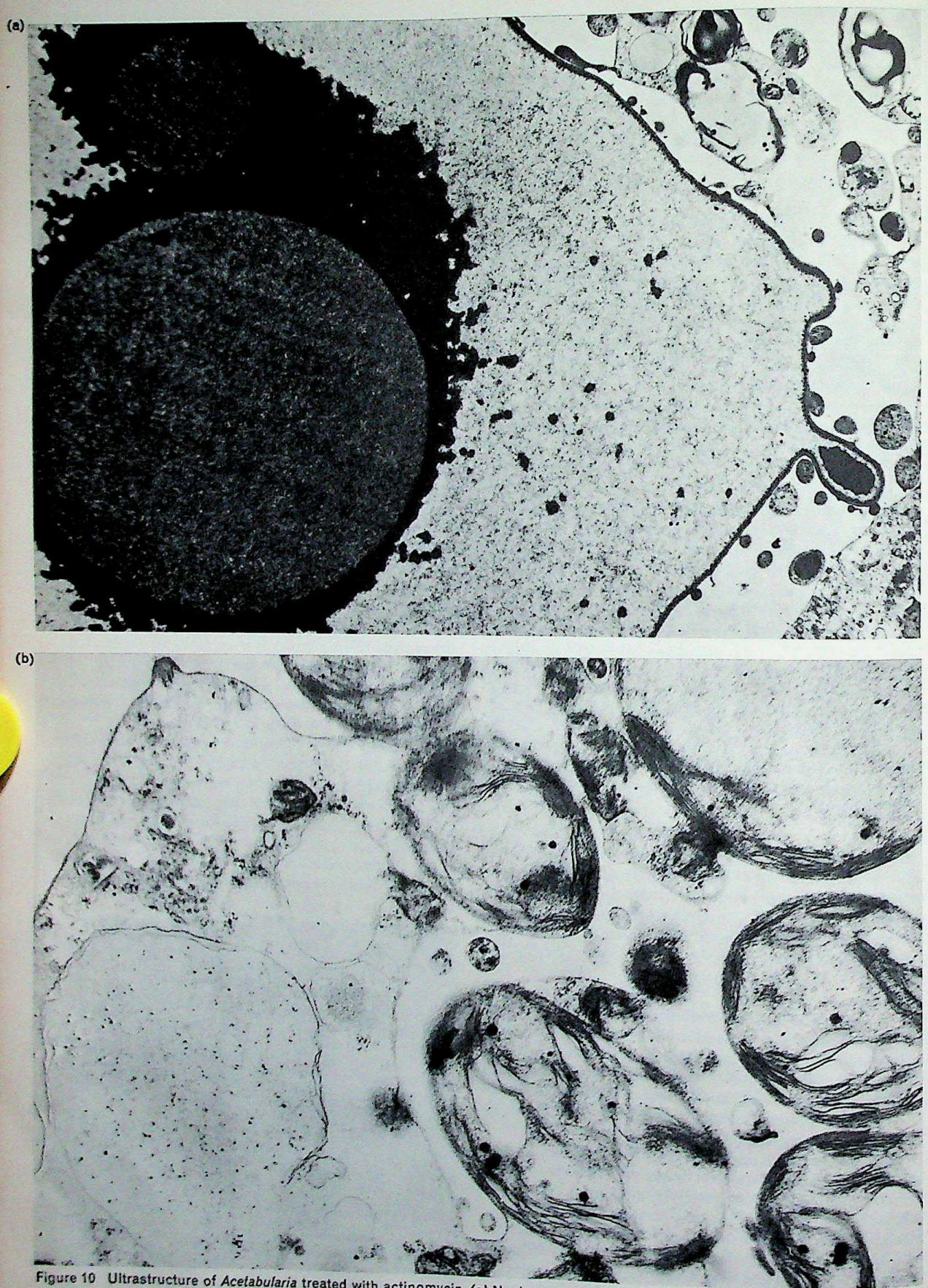


Figure 10 Ultrastructure of *Acetabularia* treated with actinomycin. *(a)* Nucleus with a fragmented nucleolus. (×8000) *(b)* Altered chloroplasts. (×21 000) (Compare with figure 5.)

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

RNA-polymerase, and can therefore produce m-RNA's, and they assemble amino acids to form proteins. The synthesis of the RNA's and that of the chloroplast proteins are both under the control of the chloroplast DNA—both are blocked if actinomycin is added to isolated chloroplasts.

If the chloroplasts on their own use the same mechanism for protein synthesis as the complete cell does, they will be to a large extent independent of the nucleus; D. Shephard, one of our collaborators, has actually shown that the number of chloroplasts in an enucleate fragment increases as the fragment regenerates. The chloroplasts thus have the striking property of being able to multiply even in the absence of a nucleus.

The nucleus as a biological clock

The role of the nucleus in biological timing can be studied effectively in *Acetabularia*. A photosynthetic rhythm—photoperiodism—that has been set up by exposing the alga to regular periods of light and dark will continue for weeks in enucleate fragments [19, 20]. However, E. Schweiger, H. G. Wallraff, and H. G. Schweige have recently shown [21] that the nucleus is actually involved in oxygen metabolism in the cytoplasm. They found that if fragments containing a nucleus were combined with enucleate ones with a different photoperiodism, it was the rhythm of the former that prevailed. In addition, T. Vanden Driessche has shown in our laboratories that the photoperiodism of complete algae is destroyed by actinomycin; DNA is therefore involved in the biological clock. These experiments show that there is a delicate interaction, not as yet understood, between the m-RNA's formed in the nucleus and the chloroplasts. Shephard's work, mentioned above, confirms this. He found that, although chloroplasts will continue to multiply after the nucleus has been removed, they do so more slowly. The nucleus thus supplies something that the chloroplasts need if they are to maintain their normal rhythm of multiplication.

These experiments, and those quoted earlier, show that the giant alga *Acetabularia mediterranea* is more than a natural curiosity. It is an ideal material for the study of the relative roles in morphogenesis of the nucleus and of cytoplasm.

References

[1] Hämmerling, J. *Roux' Arch. Entwicklungsmech.*, 131, 1, 1934.
[2] *Idem. Int. Rev. Cytol.*, 2, 475, 1953.
[3] *Idem. Symp. Soc. exp. Biol.*, 17, 127, 1963.
[4] Puiseux-Dao, S. *Année biol.* 11, section 3, 4, 1963.
[5] Crawley, J. C. W. *Expl Cell Res.*, 35, 496, 1964.
[6] Keck, C. in 'Methods in Cell Physiology' (edited by D. M. Prescott), p. 189. Academic Press, New York. 1964.
[7] Stich, H. *Z. Naturf.*, 6b, 319, 1951.
[8] Brachet, J., Chantrenne, H., and Vanderhaeghe, F. *Biochim. biophys. Acta*, 18, 544, 1955.
[9] Brachet, J. and Lang, K. *Handb. PflPhysiol.* 15, 1, 1965.
[10] Brachet, J. in 'Progress in Biophysics' (edited by J. A. V. Butler and H. E. Huxley). (In press.)
[11] Baltus, E. and Brachet, J. *Biochim. biophys. Acta*, 76, 490, 1963.
[12] Gibor, A. and Izawa, S. *Proc. natn. Acad. Sci.*, 50, 1164, 1963.
[13] Stich, H. and Plaut, W. *J. biophys. biochem. Cytol.*, 4, 119, 1958.
[14] Brachet, J., Denis, H., and de Vitry, F. *Devl Biol.*, 9, 398, 1964.
[15] Zetsche, K. *Z. Naturf.*, 19b, 751, 1964.
[16] de Vitry, F. *C. r. hebd. Séanc. Acad. Sci., Paris*, 258, 4829, 1964.
[17] Brachet, J. and Goffeau, A. *Ibid.*, 259, 2899, 1964.
[18] Schweiger, H. G. and Berger, S. *Biochim. biophys. Acta*, 87, 533, 1964.
[19] Richter, G. *Z. Naturf.*, 18b, 1085, 1963.
[20] Schweiger, E., Walraff, H. G., and Schweiger, H. G. *Ibid.*, 19b, 499, 1964.
[21] *Idem. Science*, 146, 658, 1964.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

The rabbit flea and hormones

Digitized by Arya Samaj Foundation Chennai and eGangotri

Miriam Rothschild

The importance of the rabbit flea as a vector for myxomatosis led to attempts, at first unsuccessful, to breed the flea in the laboratory. This article describes the experiments with the rabbit flea that showed that the life-cycle of the flea is dependent upon the hormone cycle of the host.

In 1953, myxomatosis, a virus disease of native rabbits of South America, reached Great Britain, and within a short period it had killed between eighty and ninety million rabbits. In Australia, where the disease had been introduced in an attempt to control these destructive animals, it was spread by winged vectors, chiefly mosquitoes. It seemed more likely that the disease was carried in Britain by the rabbit flea (*Spilopsyllus cuniculi* Dale) [1], which does not occur in Australia but is present on all populations of rabbits on the mainland of Great Britain.

When it was proved beyond reasonable doubt that this supposition was correct, it became evident that further information was required about the rabbit flea. It was important to study myxomatosis with the object of obtaining a better understanding of the epidemiology of the disease [2], and also of big, insect-borne epizootics in general. In Australia, attenuated strains of the virus had appeared and the rabbits had evolved immunity and resistance to the disease. With a flea vector, would events follow a similar course in Britain?

In order to investigate these possibilities, we needed to breed the parasite, as well as the host, in the laboratory. The problem was tackled in two ways: firstly by observations made on fleas on wild rabbits; and secondly by observations and experiments carried out in the laboratory, using domestic rabbits. It is usually a fairly simple matter to breed fleas on captive hosts: for example, the oriental rat flea *Xenopsylla cheopis* Roths, the most effective vector of bubonic plague, presents no problem in this respect; all it requires to initiate copulation and egg-laying is a blood meal [3]. The hen flea *Ceratophyllus gallinae* pairs and is successfully fertilized even without a blood meal, and before it shows any signs of maturation. A slight rise in temperature is an adequate stimulus. The eggs develop subsequently after a blood meal on a bird, or even on a 'wrong' host, such as man. The rabbit flea, on the other hand, lived for months on the host in the laboratory, but did not mature, pair, or lay eggs. It was eventually discovered that this species appears to be an exception among insect parasites, since its breeding cycle is dependent on the hormone cycle of its vertebrate host. By this link the two cycles are perfectly synchronized in nature.

The principal experiments

When work on the life-cycle began, we were baffled by the fact that the fleas failed to breed, although they lived for many months, including those of the spring and summer, on our rabbits in the laboratory. Yet in the wild, we found the eggs and larvae in the rabbit's nest, which showed that they were breeding at the same time as their host. Was the laboratory failure due to the lack of some subtle factor found in nature, such as changes in temperature or humidity, or in hours of sunlight; or was it due to an increase in vitamins in the host's natural diet, or to the special conditions that existed in burrows? The fact that fleas of both sexes lived side by side, ingesting copious blood meals, and yet did not attempt copulation, gave us the first clue to the solution of this problem. It was postulated that some sudden change in the blood of the host was required to activate the male and trigger off the impulse to pair. A little reflection indicated that the sex hormones of the host fulfilled the theoretical requirements of such a factor. A. R. Mead-Briggs and A. J. B. Rudge [4] followed up this idea, and demonstrated that the ovaries of the female rabbit flea matured only on pregnant does. This discovery gave great encouragement to the hormone theory, and switched our attention to the female, rather than the male, flea.

The number of hormones that could be involved in such a trigger mechanism was obviously considerable, and it was necessary to design an experiment that would eliminate as many as possible of the irrelevant factors simultaneously, while confirming the role of the mammalian sex hormones in the maturation of the flea.

About 150 freshly emerged fleas were introduced on to a normal female rabbit, which was then mated to a sterilized (vasectomized) buck. Copulation between the rabbits induced ovulation in the doe, and a pseudo-pregnancy followed. The ovaries of the female fleas matured on the fourteenth day [5]. This simple but important experiment showed that the placental hormones and the foetuses could be eliminated from our calculations; yet at the same time it confirmed that the hormones concerned with pregnancy in the rabbit were also concerned with maturation of the female flea and with certain important physiological changes which took place simultaneously in the male flea. The next experiment involved injecting an extract of the entire anterior lobe of the pituitary gland (a commercial preparation, Ambinon B) into a castrated buck rabbit. The ovaries of fleas feeding on this rabbit matured (figures 5 and 6), and the parasites laid sterile eggs (figure 8) on the seventh day.

It was now necessary to find out if maturation was stimulated in the flea by one of the six main polypeptide or protein hormones—such as prolactin, luteinizing hormone, and thyrotrophic hormone—of the anterior lobe, or whether the stimulus was provided by these hormones acting on target organs in the rabbit, such as the gonads and the adrenal glands, which in turn secreted the relevant steroids, such as progesterone, the oestrogens, and the corticosteroids. In a typical experiment, an ovariectomized rabbit was injected with luteinizing hormone. Since the target organs—the ovaries—had been removed, any response on the part of the fleas would

Miriam Rothschild

Was born at Ashton, Peterborough, in 1908, and educated at home; she passed no public examinations and holds no degree. She is an amateur naturalist, and her principal research interest is in parasitology.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

have indicated that it was this polypeptide hormone itself which was influencing maturation. In the normal entire doe, the luteinizing hormone would have stimulated the corpora lutea of the ovaries to secrete progesterone, and the response of the flea could have been to either hormone. The luteinizing hormone failed to elicit any response and could henceforth be disregarded as a primary factor causing maturation. All the experiments consisted basically of a series of trial and error assays, using freshly emerged fleas, various hormones, and castrated, ovariectomized, and thyroidectomized hosts, and hosts in which the temperature and blood pressure had been raised or lowered artificially. Eventually it was shown [5] that the most effective hormones controlling maturation in the rabbit flea are the corticosteroids (figures 5 and 10), produced by the adrenal glands under the control of the adrenocorticotrophic hormones, secreted in their turn by the anterior lobe of the pituitary. Oestradiol also exerts an influence on maturation and the ovarian cycle in the flea. Furthermore, large doses of thyroxine (a hormone secreted by the thyroid gland in response to the thyrotrophic hormone from the pituitary gland) when injected into the rabbit can induce maturation in the rabbit flea [5]. But since it was also found that the parasite can mature and lay eggs on thyroidectomized rabbits, it seemed fairly likely that thyroxine acts indirectly, by boosting the metabolism and stimulating the adrenal glands to secrete more corticosteroids. However, a maturing flea normally develops an accelerated defaecation rate, and this was not shown by those reared on the thyroidectomized rabbits, nor by those fed on rabbits given very small doses of hydrocortisone. It is therefore obvious that in nature more than one hormone is involved, directly or indirectly, in the maturation of these fleas.

Up to this stage we were still under the impression that the effect on the parasites was produced by the hormones through their effect on the rabbit. Thus we assumed that the rise in the hormone levels in the host affected its metabolism, which in turn might have raised its blood temperature, blood pressure, the level of antibodies in the blood, or some other factor in the blood stream, or even the smell or skin texture. Any of these factors, it was thought, might trigger off the secretion of the fleas' own hormones, which were presumably required, as in other insects, for maturation and the control of reproduction.

In order to throw some light on this aspect of the problem it would have been useful to feed the fleas artificially, through a membrane, adding the various hormones one at a time to their diet, instead of keeping them on a living animal. The rabbit flea, however, is not a good subject for membrane feeding, and the hormones were therefore sprayed directly on to the fleas, which were subsequently introduced on to castrated buck rabbits. It was thus shown that the corticosteroids, and to a lesser degree the oestrogens, exert a direct effect on the rabbit flea. The sprayed fleas mature and lay eggs (displaying the associated 'maturation' changes in the salivary glands, gut, and defecation rates); in addition they remain gravid for relatively very long periods (figure 3). Presumably the hormones are absorbed slowly but continuously through the cuticle. It also became clear from these experiments that, quite apart from the quantity of mammalian hormones absorbed by the flea, nutrition plays an important role in maturation. Hormone-sprayed fleas that fed steadily matured more rapidly and, attained a larger size, than those whose feeding was interrupted or disturbed for one reason or another.

Behaviour of rabbit fleas

The experiments with hormones gave us a clearer understanding of the behaviour of this highly adapted parasite. When freshly emerged rabbit fleas first find a host, they spend about three weeks on the rabbit's muzzle and cheeks, feeding at the base of the whiskers. They then move to the ears, where they fix themselves to the skin of the host by their serrated mouthparts. During the spring and summer months they remain in small groups of about 10–150 specimens in this position, causing a slight but definite irritation to the host's skin (figure 1); if the weather becomes very cold they shift to more protected sites where the fur is longer [6].

Unless the rabbit becomes pregnant, these fleas cannot breed; the chances of their finding a pregnant host are increased by their tendency to transfer to other rabbits that come into close contact with their own host, especially during copulation, play, mutual grooming, or resting together in a confined space, such as a burrow. Fleas tend to mass on pregnant does [7], and our experiments suggest that the raised level of hormones induces them to fix more firmly, and that once they have found such a host, they do not readily detach themselves. During the last ten days of the rabbit's pregnancy, the level of hormones in the host's blood rises sufficiently to initiate the process of maturation in the fleas. This involves a series of profound changes (figures 5 and 6) in the whole organism, which include increased development and enlargement of the salivary glands; an overall increase in size of the gut, with proliferation and growth of the cells lining the midgut; secretion of yolk and maturation of the oocytes; secretion of an egg-shell coating material in the pedicels of the ovarioles; development of the spermatozoa; and increased defecation rate. In the male these changes, although well marked, are not so dramatic as in the female. Thus the salivary glands and cells lining the midgut do not reach the size of those in the female, and the maximum defecation rate of the male is one blood squirt every four minutes—the normal rate is one every fifteen to thirty minutes—whereas in the female, during the last days of the host's pregnancy, it can attain a rate of one squirt per minute. Yolk formation in the female is definitely dependent on the hormone levels associated with the breeding cycle of the rabbit, but it is not yet clear exactly how far sperm development can progress on a non-pregnant adult host.

It is interesting that the level of the hormones in the blood of the host controls not only the process of yolk formation, but also the speed of development and the number of eggs ripening simultaneously. Thus, in nature, there is a gradual and steady development linked to the increasing volume of corticosteroids in the circulation of the pregnant doe, but this can be accelerated by injecting hydrocortisone or corticosterone, or massive doses of oestradiol, into the rabbit.

In nature, the fleas do not pair on the adult rabbit. Fleas may often be observed laying eggs while still fixed to the prepartum doe, but these eggs will be sterile (figure 2). A few hours after the rabbit has given birth, the fleas detach themselves from the ears of the doe and

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

move into the fur on her face and head. As the adult rabbit tends the newborn ones, the fleas transfer to them, and pairing then takes place. It has been found that whereas a small injection of hydrocortisone into the host will induce the fleas, especially the females, to fix more firmly to the host, a bigger dose causes them to detach themselves and run about freely in the fur on the host's head. It is therefore likely that there are hormone changes in the blood of the doe some hours after she has given birth which account for the changes in the behaviour of the fleas.

Once on the newborn young, the fleas feed avidly. They spread themselves somewhat generally about the body, but prefer the sacral region, and the back and flanks above the tail. Pairing occurs after a few hours. The factor that induces copulation of the fleas is at its maximum in the day-old rabbit, and thereafter wanes, until it disappears when the young are 7–8 days old.

It is now known that the corticosteroid level in the blood of the newborn young rabbits is considerably higher than in the pregnant doe [8], but although this high level is presumably responsible for the increase in the speed of maturation of fleas observed feeding on newborn young [9], it is not responsible for pairing. Fleas do not, for instance, pair on shaved 8-day-old rabbits that have had their corticosteroid level raised above that found in a day-old rabbit. The factor, whatever it may be, influences the female to stimulate the male and then accept copulation. A male flea which has not yet fed on the newborn young, and in which sperm have not reached their maximum stage of development, will nevertheless succeed in copulating with an immature female, providing she has already spent some hours feeding on the baby rabbit. Yet a male flea, either fixed, or free alongside fully matured females on a pregnant doe, or on a rabbit whose corticosteroid level has been greatly increased with injections, makes no attempt to pair. It seems possible that the female flea, after feeding on the newborn young rabbit, becomes receptive herself, and releases a volatile attractant which stimulates the male and draws him to her. His approach to her at this stage is very characteristic: he follows a markedly zig-zag course and then quickly slips beneath her and tips up the abdomen. Both sexes feed while pairing.

At this time the defecation rate is at its maximum. The liquid blood which is passed out of the anus gradually dries and it ultimately falls into the nest. Here it becomes an important element in the diet of the larvae that will eventually develop in the nest debris.

The fleas leave the body of the young rabbit after pairing and generally lay their eggs in the bottom of the nest. The egg, larval, and pupal stages are completed in about 30 days, by which time the nestling rabbits have usually left the breeding place. At the age of approximately three weeks, baby rabbits become unattractive to fleas. This is an adaptation that avoids both over-infestation and the risk, as far as the parasite is concerned, of 'killing the goose'. If, however, the doe has a second litter in the same breeding place, which occasionally occurs, these young rabbits are battened on by the generation of hungry fleas already in the nest, and these can reach the egg-laying stage within two or three days. In nature, second brood nests of young have been found containing thousands of fleas; how much damage they inflict on the baby rabbits is not known.

Figure 1 A group of male and female rabbit fleas feeding on the inside of a rabbit's ear. Note the patches of inflamed skin where the fleas are attached. (×7)

Figure 2 Fleas under the influence of mammalian hormones laying sterile eggs on the host. Note the blood spattering the hairs. This has recently been passed out of the anus of the flea. The striped appearance of the fleas is due to the distension of the gravid abdomen. (×8)

Figure 3 Large gravid flea which has been sprayed externally with hydrocortisone. Note the relatively small male in the foreground. (×15)

Figure 4 Section through part of an ovariole of a flea which has returned to the doe after egg-laying in the nest. The bright red nucleus is at the centre of a resorbing oocyte. The circular blue patch is one of the 'blue bodies', a connective-tissue attachment in the wall of the pedicel. After the eggs are laid, these frequently remain in the base of the ovarioles or ovaries of spent fleas and can then give an indication of the number of eggs already laid. (×450)

Figure 5 Section through the abdomen of a flea that was feeding on a rabbit which had been injected with hydrocortisone. The yolk globules in the developing oocytes are stained bright red. The greyish egg-shaped body is one of the salivary glands which enlarge under the influence of the hormones. (×120)

Figure 6 Section through the abdomen showing elongation of the villi of the mid-gut epithelium. To the left are several developing oocytes. The pedicel of the ovarioles can be seen at the base of the mid-gut, showing its yellow secretion which is one of the earliest manifestations of maturation. This secretion can be detected in the lumen of the pedicels six hours after moving a flea from a normal buck on to a day-old rabbit. (×170)

Meanwhile the parent fleas, after a period, which varies from 4–20 days, of pairing and egg-laying in the nest, return to the doe. This sudden desertion of the young in favour of the mother is not understood. It may be due to yet another change in the relative hormone levels in the blood of the two age groups, but this is speculation. Curiously enough, the fleas frequently return to the doe long before they are spent, the males with testes still containing many sperm, and the females with sperm still stored, apparently normally, in their spermathecae and with developing eggs in their ovarioles. But once the fleas are settled back on the doe, the eggs are rapidly resorbed and the young developing oocytes are arrested at an early stage, before yolk formation; the salivary glands in both sexes regress; and the midgut epithelium and the secretory epithelium of the pedicels return to the form seen before maturation. Females in which the changes have taken place reveal they have laid eggs by the presence of degenerating egg follicles (corpus luteum) in the ovarioles and of 'blue bodies', which are areas of connective tissue below the site of attachment of the proximal oocytes (figure 4). Should the doe become pregnant again, these fleas can, in response to the rise in the hormone level, commence a new breeding cycle, although their reaction is slower than that of virgin fleas. Since fewer males are found to be available at this stage, it is assumed that a fairly high proportion die in the nest after pairing.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

1

2

3

4

5

6

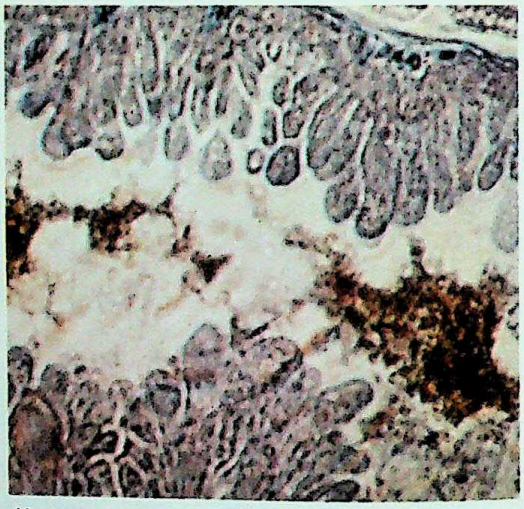
All photographs by M. Rothschild

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

7

8



10

9

11

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Figure 7 Section through the testes of a freshly emerged flea. The sperms are still relatively undeveloped, and the 'heads' are undifferentiated and confined in their hyaline cysts. (×530)

Figure 8 Blood passing through the proventriculus of a flea into the mid-gut. Note the strong chitinous spines. (×560)

Figure 9 Section through the testes, showing sperm with heads differentiated but still only partly developed. Testes of fleas which are fully matured appear in section as a tight mass of sperm in which there are no spaces and in which it is impossible to trace the course of a single sperm. (×670)

Figure 10 Epithelial cells lining the mid-gut developing under the influence of ACTH, with which the host had been injected. (×440)

Figure 11 Section through the terminal portion of a developing egg seven days after an injection of 'Ambinon B' into the host. Note the egg-shell (chorion) is already well developed. The tiny holes at the anterior end are the micropyles. (×400)

It is striking that there is no spermatogenesis in the adult flea, and that when the flea emerges from the pupa, the testes already carry their full complement of sperm. Once used up there is no replacement. Although the flea's spermatozoa grow and develop while on the host (figures 7, 9), no new sperms are formed. The pattern is different for the female, since eggs can be developed from the germarium of each ovariole practically throughout the life of the adult.

Comparison with other species of flea

It is clear that the rather specialized breeding habits of the rabbit, combined with the specialized feeding habits of the rabbit flea, have placed a premium on the linking of the two sexual cycles. By their response to these hormones in the host, the fleas are guaranteed their breeding habitat. They are transported by the doe to her nest, which is frequently constructed away from the main warren, and by their reactions to the rise and fall in the levels of corticosteroid and other hormones in the host they are induced to leave the doe at the critical moments following parturition, and to lay their eggs in the nest with the newborn young. The food supply is thus guaranteed for their own developmental stages, which are spent in the nest.

In nature there are probably other parasites which respond to the sexual cycle of the vertebrate host, especially the internal worm parasites, but among fleas the most likely group in which to seek a parallel phenomenon are bat fleas of the genus *Ischnopsyllus* Westwood. In the spring certain species of bats leave their winter quarters and the females repair to special summer breeding roosts on their own. It has been noticed [10] that before the bats depart, the fleas crowd on to the females. This clue is well worth following up.

It was thought at one time that perhaps all fleas required a certain level of corticosteroids in the blood of their host for successful breeding, and that the only feature peculiar to the rabbit flea was that it had become geared to the higher levels characteristic of pregnancy. However, this surmise proved to be incorrect, since the oriental rat flea *Xenopsylla cheopis* Roths. will breed on hypophysectomized rats [11].

Corticosteroid levels in the host

The only insect known to be sensitive to the corticosteroids in the blood of the host is the rabbit flea, which responds to the minuscule dose of 16 μg of hydrocortisone injected into a 10 lb rabbit. The flea's reactions and behaviour on the host indicate that there is a steady rise in the level of corticosterone in the rabbit's blood during the last 10 days of the host's pregnancy, possibly a further short rise in the first few hours following parturition, and thereafter a decline to normal prepartum levels. The flea also indicates (by rapid maturation and restlessness) that the level of corticosteroids in the blood of the newborn rabbits must be at least twice as high as in the doe, and that in 3–5-week-old rabbits, on the contrary, it must drop to a lower level than at any other time of their lives. Since our experiments showed that the flea is much more sensitive to hydrocortisone than corticosterone, its behaviour on the baby rabbits suggests that perhaps hydrocortisone may be present in the young (one to six days old), although it has not hitherto been detected in measurable quantities in adult rabbits.

We have often noticed that when the young are born dead or are feeble—and about 50 per cent of winter litters are non-viable—the fleas fail to leave the doe after parturition. This suggests that the hormone level in the blood is not raised sufficiently to stimulate detachment from the ears of the host. It is possible that hormone imbalance may be one of the factors adversely affecting the young rabbits in the winter litters. Furthermore, it has been found that the ovaries of fleas feeding on rabbits suffering from myxomatosis [14] also mature, even though the rabbits are not pregnant. This may be due to a stress reaction in the diseased host which in turn raises the level of the corticosteroids in its blood.

Mechanism of action

It is, of course, not known how the mammalian hormones produce their effect on the rabbit flea. The investigation of maturation—the secretion of yolk and the various changes which culminate in egg production and fertilization—has revealed that a very complex system controls these activities in insects. V. B. Wigglesworth has concluded [12, 13] that neurosecretory cells in the brain (protocerebrum) and suboesophageal ganglion, the corpus allatum and corpus cardiacum, and the ovary, are all involved in this process. They influence one another by nervous stimuli, by neurosecretions carried along nerve pathways, and by humoral factors circulating in the blood. He pointed out that the relative parts played by the different elements in this system vary from one insect to another.

One of the most important factors involved in insect maturation is the secretion of the so-called juvenile or yolk-producing hormone, the action of which is reproduced by farnesol [13]. It has been found that, in nature, a wide variety of stimuli, ranging from distension of the abdomen with blood, to the act of copulation, can initiate the secretion or release of stores of this hormone into the body tissues. It may well be that in the rabbit flea there is a direct relationship between the mammalian hormones and the secretion and release of the juvenile hormone, or possibly of the hormone from the neurosecretory cells of the brain. When the corticosteroid level in the blood of the host is high, it would seem that the juvenile hormone levels are also high, and that these fall off correspondingly

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

when the mammalian hormone is withdrawn or when its level in the blood is reduced. Fleas sectioned after they have spent a period of 6–24 hours feeding on the newborn young, in which the corticosteroid levels are at a maximum in the rabbit, demonstrate that various changes associated with maturation are occurring simultaneously in different organs. However, experiments have also shown that not all the organs in the flea respond to the same levels of hormones. Thus, for example, relatively low doses of corticosteroids result in yolk formation and ovariole secretions, but much higher levels, characteristic in nature of those associated with the last days of pregnancy and the first day of life, are required to produce the highest defecation rates in the fleas. Furthermore, small doses induce them to feed steadily, whereas very large doses make them restless and intermittent feeders. This in turn slows down maturation.

It is, of course, possible that this flea has now progressed so far along the parasitic road to dependence that it has lost the power of secreting its own hormones and has to make use of the mammalian hormones themselves. This is unlikely, since, during the larval stages, the flea requires secretions of the juvenile hormone without which the insect would undergo precocious metamorphosis [13]. It is extremely improbable that the larval fleas would have to rely for their supply of this hormone on the blood of the host, passing out of the anus of the parent flea. It seems more reasonable to suppose that the flea can still secrete its own juvenile hormone but that its release is under the influence of the hormonal blood levels of the rabbit. This is certainly one of the more interesting aspects in the life of the rabbit flea and is worthy of investigation. Unfortunately, since the advent of myxomatosis and the reduction in the numbers of its host, the rabbit flea has become relatively scarce. Furthermore, it is not easy to handle, and these considerations make an early solution of the problem rather unlikely.

Acknowledgments

I gratefully acknowledge the help and assistance of Mr B. Ford, Professor G. W. Harris, and Dr D. Exley of the Department of Human Anatomy, University of Oxford. I would also like to thank Dr V. Wilson and Mr R. Lawrence of the Roussel Laboratories for designing the sprays for spraying the fleas with hormones, and Mrs Barbara Luke of the Department of Zoology, University of Oxford, for her assistance with figure 11.

References

[1] Rothschild, M. 'Report to the Myxomatosis Advisory Committee'. 1953. (Private circulation.)
[2] Andrewes, C. H. *Nature, Lond.*, 174, 529, 1954.
[3] Suter, P. R. *Acta trop.*, 21, 193, 1964.
[4] Mead-Briggs, A. R. and Rudge, A. J. B. *Nature, Lond.*, 187, 1136, 1960.
[5] Rothschild, M. and Ford, B. *Ibid.*, 201, 103; 203, 210, 1964.
[6] *Idem.* 'Movements of the Rabbit Flea (*Spilopsyllus cuniculi* Dale) on the Captive Host'. 1st Cong. Parasitology, Rome. September 1964.
[7] Allan, R. M. *Proc. R. ent. Soc. Lond.* (*A*), 31, 145, 1956.
[8] Exley, D., Ford, B., and Rothschild, M. (In preparation.)
[9] Mead-Briggs, A. R. *J. exp. Biol.*, 41, 371, 1964.
[10] Hurka, K. *Acta faun. ent. Mus. nat. Pragae*, 9, 57, 1963.
[11] Rothschild, M. and Ford, B. *Proc. R. ent. Soc. Lond.* (*C*), 29, 35, 1964.
[12] Wigglesworth, V. B. *Endeavour*, 24, 21, 1965.
[13] *Idem.* In 'Advances in Insect Physiology', Vol. II, pp. 299, 302, 1964.
[14] Rothschild, M. and Ford, B. 'Reproductive Hormones of the Host Controlling the Sexual Cycle of the Rabbit Flea (*Spilopsyllus cuniculi* Dale)', XII International Congress of Entomology, London. 1965.

Book reviews

LATTICE THEORY

Introduction to Lattice Theory, by D. E. Rutherford. Pp. x+117. Oliver and Boyd Ltd, Edinburgh and London. 1965. 35s. net.

The aim of this elegant and well-written little book is to present the basic ideas of lattice theory to beginners in the subject. However, although the book demands no previous technical knowledge, a reader who is not already trained to receive modern abstract mathematics in general, and modern algebra in particular, is unlikely to make much of it. With this proviso, one can say that the job has been well done: the monograph deals briefly with a fair number of topics, above all the Boolean algebras and their various applications to formal logic and the theory of switching circuits. There are also accounts of Brouwer algebras, intuitionist logic, topology, and metric spaces. The author's claim to treat algebraic geometry as well as the rest is a very slender one: the whole lot is knocked off in a couple of pages. This may indeed be a formalist's notion of what the topic comprises, but it is far from being a geometer's.

The general production of the book is excellent. For those who can take it, the work is warmly welcomed. *L. Roth*

ELEMENTARY PARTICLES

The Eightfold Way, by Murray Gell-Mann and Yuval Ne'eman. Pp. xi+317. W. A. Benjamin Inc., New York and Amsterdam. 1964. Paper, $4.35; cloth, $8.80.

Over the last few years, our list of strongly interacting particles (the 'hadrons') has been increasing at a considerable rate with the continuing discovery of further particle states, and it has become clear that the hadronic states occur grouped in characteristic patterns of charge multiplets. These octet and decimet patterns correspond to a unitary (or SU(3)) symmetry for the hadronic interactions, and its recognition has been the most significant development to date in our knowledge of the hadrons and their strong interactions. This unitary symmetry represents a generalization of the charge independence property (equivalent to an SU(2) symmetry) which has been known for nucleons and nuclear states for several decades.

This volume collects together a large fraction of the basic papers on SU(3) symmetry and its implications for elementary particle states. The papers are grouped into chapters, for example on the mass formula, supermultiplet assignments, the symmetry-breaking interactions, and on the SU(3) properties of the electromagnetic and weak interactions. The authors have prefaced each chapter by a few pages of introduction to set the scene and to direct the reader's attention to further papers which elaborate particular topics. Every scientist interested in the properties of the elementary particles will wish to have this important collection of papers on his bookshelf, close at hand for easy reference. The reviewer has found himself referring to it many times every day. *R. H. Dalitz*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

THERMODYNAMICS

Classical Thermodynamics of Non-electrolyte Solutions, *by H. C. Van Ness. Pp. viii+166. Pergamon Press, Oxford. 1964. 40s. net.*

The object of this book is the determination of thermodynamic data from experimental measurements. The scope includes constant-composition fluids, partial molal properties, and vapour-liquid equilibria. This seems a small field of application, and yet the author approaches his topic with a directness and completeness that any student who has previously waded through the vague mathematical uncertainties of many a textbook on thermodynamics will appreciate. Before embarking upon the consideration of experimental data, the author deals with the thermodynamic properties of fluids. It is pleasing to find thermodynamics treated as a set of postulates from which, through mathematical manipulation of a rigorous and defined nature, useful relationships between measurable quantities may be obtained.

The constant-composition fluid section gives considerable emphasis to the virial formulation of the equation of state. A more detailed account of the theory of corresponding states might have been expected.

The thermodynamic properties of mixtures and the partial molal properties of many-component systems are also well developed, and this, together with the discussion of the tests of thermodynamic consistency, provides a valuable basis for the student dealing with either raw data from the literature or his own laboratory data.

The final section deals with vapour-liquid equilibria and emphasizes the value of the determination of the activity coefficient. The section on the calculation of vapour-pressure equilibria from vapour-pressure data is most valuable from a utilitarian point of view. It is a pity that partially miscible liquids are treated only briefly at the end.

In a book dealing with the interpretation of experimental data it is unfortunate that more reference to pertinent experimental studies has not been made.

J. Walkley

ELECTRONICS

Physical Electronics, *by G. F. Alfrey. Pp. 220. D. Van Nostrand Co. Ltd, London. 1964. Paper bound, 27s. 6d. net; cloth bound, 50s. net.*

This book treats a great variety of subjects, such as the electron structure of atoms and of solids, electron emission, electron optics, electron conduction in gases and in solids, plasma physics, transistors, magnetism, dielectrics, noise, and lasers. As the author tries to cover all this in 200-odd pages, one cannot be surprised that the treatment is sketchy.

The contents are not very well balanced. Thus the electron microscope is described in two pages, but the same space is given to the description of the far less important thyratron. Moreover, half a page is devoted to sodium and mercury lamps and again half a page to an attempt to explain the Bloch solution of Schrödinger's equation. The text contains a number of minor errors—for example, the Boltzmann constant k is printed throughout the book as a vector in heavy type. Clausius-Mossotti is several times misspelled as Clausius-Misoti. The electron orbits in Fig. 5.2 are wrong; they should be made divergent by one-half of the lens.

This book could not, despite the statement on the dust cover, be recommended as a basic text to physics undergraduates. It might, however, be quite useful for somebody who wants to get some information about the scope of this extensive subject.

O. E. Klemperer

ELECTRON MICROSCOPY

An Introduction to the Fine Structure of Cells and Tissues, *by Keith R. Porter and Mary A. Bonneville. (Second edition.) 37 illustrations. Henry Kimpton, London. 1964. Cloth bound 56s. net., student edition, 34s. net.*

This book contains 32 electron micrographs, each followed by a page or two of description with key references. It aims to provide students with the information about the fine structure of various cells that has come from electron microscopy, and thus to serve as a supplement to the standard textbooks.

The first edition of this book was justifiably popular, and in the second edition both pictures and text are brought up to date. The pictures are original and at least as good as any that have yet been published. Each is reproduced full-page (28 × 20 cm), which is larger than is normally possible in a journal. This allows a magnification that does justice to the fine structure without losing the context of the whole cell in which it is placed. The text is clear, concise, and authoritative.

The printers have done a splendid job at a reasonable price, and the cheaper student edition is particularly good value. But this is not only a book for students; any histologist will be delighted by this beautiful collection of pictures.

Robin C. Valentine

SOLID-STATE PHYSICS

Symmetry and Magnetism, *by Robert R. Birss. Pp. xx+252. North-Holland Publishing Co., Amsterdam. 1964. 60s. net.*

This book is the third volume in a series of monographs on selected topics in solid-state physics, and it is one which appeals specially to all who are interested in either magnetism or in solid-state physics in general. It is based primarily on mathematical-physical developments, made by Soviet scientists in recent years, which the author describes and discusses in a very penetrating manner.

We are used to dealing with 32 classes of crystals and appreciate that 230 spatial symmetries can be obtained from them. But when ferromagnetic, ferrimagnetic, and antiferromagnetic crystals are considered, the orderly distributions of the spin magnetic moments and their directions introduce 1191 additional magnetic space groups whose description in a convenient scheme is important.

The author devotes much attention to the concept of symmetry in space-time and its importance in the specification of the symmetry of magnetic and non-magnetic crystals and in the simplification of the forms of the tensors which represent the various macroscopic physical properties of crystals. In particular, he gives valuable discussions of applications to problems of magnetocrystalline anisotropy, magnetostriction, and galvanomagnetic effects. His book, though excellently written, is not an easy one to read, but it is very stimulating.

L. F. Bates

CHEMISTRY

Annual Reports on the Progress of Chemistry for 1963. *Vol. LX. Pp. 681. The Chemical Society, London. 1964. £2 net.*

At a time when the amount of chemical publication is increasing exponentially, it is surprising to find this one-volume annual review retaining its prestige. Moreover, the present volume is less than 50 per cent larger than that for 1933. We have numerous stages of condensation of published chemical research in abstracts, review journals, and reports on progress in specific fields, and for the broad subdivisions of physical, inorganic, organic, and biological chemistry. There still remains a demand for the present inclusive review, which deals with seven major topics in physical chemistry, three in inorganic, twelve in organic, and four each in biological and analytical chemistry. There is a final section dealing with structures of inorganic and organic molecules determined by crystallographic study.

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

At this degree of condensation the product can no longer be said to be the 'cream' of the literature. It corresponds rather to a mineral concentrate in which each observer, from his individual viewpoint, is aware of different items by their brilliant sparkle. The Reports provide an obvious service to the university lecturer whose teaching commitments cover a much broader range than his field of research. This volume is a worthy successor to those of previous years.

A. N. Hambly

ANALYTICAL CHEMISTRY

New Methods of Analytical Chemistry, *by R. Belcher and C. L. Wilson in association with T. S. West. (Second edition.) Pp. xv+366. Chapman and Hall Ltd, London. 1964. 60s. net.*

This book is a most valuable review of recent developments in what has come to be called classical analytical chemistry. In addition to an authoritative survey of titrimetric and gravimetric methods, it gives a useful account of solvent extraction methods and selective reagents for spectrophotometry, and an eclectic compilation of procedures. The author index bears witness to the remarkable productivity of the British research schools, and underlines the pre-eminence of the authors in this field.

Although the authors state in the preface that their intention was to show that novelty in analytical techniques is not necessarily synonymous with the use of an instrumental method, their book is likely to prove a most fruitful source of ideas for the instrumentalists. Instruments are no better than the chemistry of the methods for which they are used, and the present trend of analytical research towards achieving a better understanding of the chemical processes involved can have only a beneficial effect on the development of analytical methods of all kinds.

This book can be unreservedly recommended as essential reading for all analytical chemists.

R. A. Chalmers

MOLECULAR SPECTRA

The Theory of the Electronic Spectra of Organic Molecules, *by J. N. Murrell. Pp. xiv+328. London: Methuen & Co. Ltd; New York: John Wiley & Sons Inc. 1963. 55s. net (U.K. only).*

Many organic chemists will have become acquainted with simple molecular orbital theory by reading Streitwieser's excellent book. If they have thought at all deeply about the theory they will probably have realized that often a more sophisticated and less empirical theoretical approach would be desirable, especially when discussing electronic spectra.

Professor Murrell has written the ideal sequel to Streitwieser, and this book presents a wide range of material in a most readable and compact form. The discussion highlights clearly the physical ideas behind these more sophisticated theories. Both the power and present limitations of the method are demonstrated in treating the straightforward electronic spectra of a diverse range of materials, and also vibrational structure, steric effects, radical and ion spectra, fluorescence, and phosphorescence. Intensities of symmetry-forbidden bands receive due mention.

This book is strongly recommended, especially to those who are steadily filling the literature with dubious correlations based on primitive molecular orbital calculations. It may be in time to stop molecular orbital theory from getting as bad a reputation as the 'resonance theory' misapplication of valence bond theory.

R. J. R. Hayward

SURFACE-ACTIVE AGENTS

Identification and Analysis of Surface-active Agents by Infrared and Chemical Methods, Text Volume and Spectra Volume, *by Dieter Hummel (translated from the German by E. A. Wulkow). Pp. xiv+386; 466 spectra. Interscience Publishers, New York, London, and Sydney. 1964. 150s. net.*

This work provides the first systematic approach to the identification and analysis of surface-active agents to incorporate both the traditional methods of chemical and ion-exchange analysis with those of infra-red spectroscopy. The work is in two volumes—one is the text, and the other consists of the spectra of 466 surface-active agents.

A system of qualitative analysis is described, based on detection and isolation of surface-active compounds in industrial products, followed by various tests to determine the main groups to which they belong, and evaluation of the infrared spectrum. Finally, there is a chapter on quantitative analysis. At the end of the text there are a number of very useful tables giving such things as systematic classifications of surface-active agents, lists of commercial products, and methods of testing.

The English translation is both concise and lucid, and the book should prove extremely useful to research workers in surface chemistry.

D. O. Hayward

CHELATE EXTRACTION

The Solvent Extraction of Metal Chelates *by Jiří Starý, edited by H. Irving. Pp. xiv+240. Pergamon Press, Oxford. 1964. 60s. net.*

The solvent extraction of metal chelates is a subject of major importance in chemistry, of value in its own right for yielding physico-chemical information on complex formation, and for its many applications in chemical separations and analysis. Dr Starý, one of the leaders of the Czech school, has made many contributions to the field, including the development (with Dr Růžička) of the principle of substoichiometric separations, which has proved to be of great significance in isotope dilution and activation analysis.

The book has the advantage of being detailed and comprehensive, as well as authoritative; yet at the same time it offers a lucid exposition of fundamentals. The properties of chelating agents and extraction systems are treated systematically and both extraction curves and extraction constants are given, from which the best conditions for separation of a desired metal can be decided. Selective extraction procedures for the isolation and determination of metals are also described in detail.

The author has performed a great service in collecting and collating the wealth of material scattered throughout the literature, much of it in articles not readily accessible to the Western world. The monograph will surely prove indispensable to all engaged in analytical chemistry.

D. F. C. Morris

TERPENE CHEMISTRY

Tetracyclic Triterpenes, *by Guy Ourisson, Pierre Crabbé, and Oscar R. Rodig. Pp. 237. Hermann Publishers Ltd, Huddersfield. 1964. £2 19s. net.*

This book is an English adaptation of a French edition by G. Ourisson and P. Crabbé: *Les triterpènes tétracycliques*, originally published in 1961. The present edition has been revised to include complete literature coverage up to July 1962, with some important results as late as June 1963.

As would be expected from authors who have contributed so much to our knowledge of tetracyclic triterpenes, the book is an authoritative review. The reactions of functional groups in rings A, B, C, D, and in the side-chain of the tetracyclic triterpene skeleton are discussed in separate sections. This presentation, rather than the more usual consideration of individual compounds, leads to a very concise and lucid

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

description of the principal reactions, which are further summarized in very clear flowsheets. Detailed cross-referencing of the text overcomes the difficulties associated with the more complex substances, in which reagents effect molecular changes at more than one reaction site. There is a brief chapter on some aspects of triterpene biochemistry, and, finally, comprehensive catalogues of the physical properties of the naturally occurring compounds and many of their derived products.

This book is strongly recommended to students, who will appreciate the concise and lucid presentation, and to specialists, who will value the lists of physical properties and the comprehensive bibliography. *J. S. E. Holker*

STEROID CHEMISTRY

Applications of N.M.R. Spectroscopy in Organic Chemistry; Illustrations from the Steroid Field, *by N. S. Bhacca and D. H. Williams. Pp. ix+198. Holden-Day Inc., San Francisco, London, and Amsterdam. 1964. $7.95.*

In the past two decades, organic chemists have increasingly relied on spectroscopic and allied instrumental analytical techniques to aid their research work. One of the newest of these is nuclear magnetic resonance (nmr) spectroscopy. This book deals with the applications of nmr spectroscopy to steroid chemistry—a field in which other spectroscopic techniques are already successfully used.

The authors wisely assume a working knowledge of nmr theory and instrumentation, and after a minimum of introduction where, for example, the effects of solvent changes on spectra are introduced, they discuss the principal features of steroid nmr spectra in turn. These are methyl resonances (one chapter) and methylene, methine, and olefine resonances (two chapters). The effects of long-range couplings, stereochemical considerations, and a more detailed discussion of solvent effects are then dealt with. The usefulness of spin decoupling and of spectra obtained with instruments of high magnetic field and radiofrequency is shown throughout the book. It has the minimum of mathematical theory and so should appeal to all practical organic chemists faced with the interpretation of spectra. *P. Bladon*

The Biosynthesis of Steroids, Terpenes, and Acetogenins, *by J. H. Richards and J. B. Hendrickson. Pp. x+416. W. A. Benjamin Inc., New York and Amsterdam. 1964. $20.35.*

The role of acetate in the biosynthesis of natural products has been extensively rationalized during the past decade. In this welcome and stimulating monograph the authors have attempted a unified presentation of the evidence for the routes from acetate both to isoprenoid molecules and to those derived from straight chains of polyketomethylene units. The introduction of the term 'acetogenin,' applied solely to the latter group, is confusing and unfortunate, and is unlikely to be generally used.

Although the literature has been covered, for the most part, to the end of 1963, some sections of the book are already obsolescent as a result of recent developments in the field. The authors were perhaps unwise to devote so much space to hypothesis and to discuss hypothesis and experimental results in separate chapters. The structures of some natural products included in the statistical survey have subsequently been shown to be incorrect, and this account thus illustrates well both the strength of the acetate hypothesis and its weakness as an aid to structure determination.

The index is adequate and the text relatively free from trivial errors; the same, unfortunately, cannot be said of the structural formulae, which, particularly in chapter 8, contain many mistakes.

It is hoped that the authors will be encouraged to revise their text and that we may look forward to an improved second edition. *J. F. Grove*

SATELLITE PHYSICS

Theory of Satellite Orbits in an Atmosphere, *by Desmond King-Hele. Pp. vi+165. Butterworths, London. 1964. 30s. net.*

The author of this book is a world leader in the exploitation of artificial satellites for scientific purposes through analysis of their orbits; the technique makes it possible to derive a wealth of information about the figure of the Earth, and the density and temperature of its outer atmosphere. King-Hele realized the possibilities at the very beginning, immediately after the launching of Sputnik 1, and has continued from that date to make major contributions. His work has been distinguished not only by its definiteness and effectiveness but by the relative simplicity of the mathematics employed. Everything has been achieved without resort to the formidable apparatus of celestial mechanics or even of analytical dynamics.

In the present work a compact account is given of the methods and some of the results obtained by King-Hele and his collaborators in analysis of atmospheric drag effects on satellite orbits. It should be readable by any physicist without much effort and should present no difficulties of comprehension to a second-year mathematical student.

As a well-written account of a remarkably successful and relatively very cheap application of artificial satellites, this book is recommended to those working in space research and also to mathematicians, physicists, and engineers interested in finding out something of what goes on, very effectively, in this field. *H. S. W. Massey*

GEOLOGY

The Phanerozoic Time-scale, *edited by W. B. Harland, A. Gilbert Smith, and B. Wilcock. Vol. 120S, A supplement to the Quarterly Journal of the Geological Society of London. Pp. viii+458+vi. Geological Society, London. 1964. £5 net. (Paperback, £4 net.)*

This new and welcome venture of the Geological Society of London gives a critical review by some thirty contributors of the present position in the radiometric dating of the fossiliferous rocks. The relations between radiometric and stratigraphical dating are examined and the limits of accuracy of the geophysical methods assessed. It may be comforting to the field geologist to be told that, at present, palaeontological correlation is superior at all levels. The methods of radiometric dating are described and their varying usefulness for the stratigraphical time-scale is indicated. Separate articles present the reliable radiometric data available for each geological period: in these, the stratigraphical controls for the samples dealt with by the geophysicist are critically assessed. The results of these exercises are summarized in an invaluable statement, to be referred to as the 'Geological Society Phanerozoic Time-scale 1964'. The volume ends with an assemblage of 337 items, which give abstracts of the data on dating, critically examined from both the radiometric and stratigraphical aspects. The editors are to be congratulated on their work on this excellent volume, which forms a worthy tribute to Professor Arthur Holmes, the doyen of British geologists active in this borderline field. *H. H. Read*

ANTARCTIC BIOLOGY

Biologie antarctique, *edited by Robert Carrick, Martin Holdgate, and Jean Prévost. Pp. 652. Hermann, Paris. 1964. 54 francs.*

This volume represents the proceedings of the first International Symposium

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

devoted to Antarctic biology held in Paris as long ago as September 1962, under the auspices of the Scientific Committee for Antarctic Research. The purposes of the symposium were 'to evaluate current research in all branches of Antarctic biology, . . . to foster international co-operation, . . . and to outline the courses that future work might follow.'

The book consists of 62 papers (only ten in French, with English summaries) grouped under 14 headings, including human physiology and psychology; animal physiology and ethology; ecology; microbiology; biogeography and taxonomy; and conservation. The papers do not set out to provide a comprehensive survey of Antarctic biology; they are reports of individual research projects, admittedly some of them preliminary. However, the discussions and reference lists of the papers in the different sections serve as a good introduction to work in progress in this field. Moreover, each section ends with some two or three pages of, in many cases, very interesting discussion by the participants of the symposium.

Clearly this book is not intended for laymen, but it provides biologists with a very wide range of information about Antarctic plants and animals. In addition, specialists who are not directly interested in Antarctic biology but who want to check whether there is work in progress relevant to their own fields can make a useful preliminary search here.

B. M. Murray

BIOLOGICAL PROCESSES

The Structure and Properties of Biomolecules and Biological Systems, *edited by J. Duchesne. Pp. xii+754. Interscience Publishers, a Division of John Wiley & Sons Ltd, London, New York and Sydney. 1964. 188s. net.*

The primary aim of this assembly of articles by various authors is the interpretation of the properties of biological systems at the molecular and electronic levels. Four articles cover the theory of electronic and quantum-mechanical aspects of proteins and nucleic acids. A further fourteen are on experimental approaches to this goal, including nuclear magnetic resonance, electron-spin resonance, electronic conductivity, infra-red spectroscopy, and enzyme-kinetic and other methods. Most of the articles are authoritative and of a very high standard. An exception is one on prospects for the use of infra-red spectroscopy, by J. Lecomte, which appears out of touch with many current developments and has no adequate references. No concessions are made to biologists, who will need considerable theoretical chemistry to get to grips with these articles. For them, and for specialists in other fields, some of the introductions to the topics are rather brief, authors tending to assume that their reasons for a particular approach are self-evident. This book is quite sobering, since it shows clearly how, with the molecular approach to biology apparently achieving great successes, we are yet far removed from understanding elementary biological systems in terms of the basic sciences. *B. R. Malcolm*

PHOTOPERIODISM

Photoperiodism and Seasonal Development of Insects, *by A. S. Danilevskii. (Translated from the Russian by J. Johnston, assisted by N. Waloff.) Pp. ix+283. Oliver & Boyd Ltd, Edinburgh and London. 1965. 70s. net.*

The extensive continuous land mass of Russia in Europe provides exceptional opportunities for studying the adaptation of single species to life at varying latitudes, and, particularly, survival during the winter months. Russian investigators have taken full advantage of these opportunities in relation to both plants and animals. The response of insects to the length of day has been examined in great detail by Professor Danilevskii and his colleagues in the Department of Zoology of the University of Leningrad. Their results, representing more than 10 years' intensive work, were brought together and, along with researches on similar lines from other parts of the world, were published in book form in Russia in 1961. The present book is a well-translated English version of that most valuable work. The approach is ecological. The induction of dormancy (diapause) in a given species in response to temperature, nutrition, and particularly to photoperiod, is considered in relation to the conditions of life. A migratory species like the cabbage butterfly *Pieris brassicae* has a set reaction which is the same in all localities; a non-migrating species such as the moth *Acronycta rumicis* constitutes a 'cline' of intergrading races adapted to different day-lengths from northern to southern latitudes. *V. B. Wigglesworth*

CYTOLOGY

The Red Blood Cell, a Comprehensive Treatise, *edited by Charles Bishop and Douglas M. Surgenor. Pp. xiv+566. Academic Press, New York and London. 1964. 121s. 6d. net.*

The authors have endeavoured to enlist the aid of a number of specialists in order to look at the whole red cell in all its aspects, though they acknowledge in their introduction that some aspects of the red blood cell have not been as well covered as might have been hoped. The most obvious gap is in the field of morphology, which is largely untouched. Apart from this defect, the book is an extremely valuable compendium of information on the chemical and physical properties of the red cell.

After a brief historical introduction, there follow excellent chapters on the composition of normal human red cells, ion and water permeability, and on overall metabolism. Other topics dealt with include haemoglobin metabolism within the red cell, life span of the red cell, and problems of red cell storage. Distributed throughout the book there are some conspicuously valuable tables which have obviously been very carefully compiled.

The book can be recommended with confidence to all who are interested in the red blood cell and its properties. It is a mine of information on a number of fields that are being actively investigated at the present time. *J. M. Yoffey*

PARASITOLOGY

General Parasitology, *by V. A. Dogiel. (Translated from the Russian by Z. Kabata.) Pp. ix+516. Oliver & Boyd Ltd, Edinburgh and London. 1964. £5 5s. net.*

This book is an extremely stimulating approach to parasitology. Originally written by the late V. A. Dogiel in 1947, this is the enlarged third edition and the first to be translated into English. The present revisers are Yu. I. Polyanski and E. M. Kheisin of Leningrad University.

It is a volume of extreme erudition and very wide knowledge. It is particularly useful to have an account of the Russian work, which is of great importance and too little known outside the Soviet Union. There are few parasitologists who will not learn some surprising facts by reading this book.

The main emphasis is laid on the so-called 'helminths' (including nematodes) and Protozoa, but other groups, such as the insects, are adequately, if not exhaustively, treated.

It is not a systematic treatise. Its main approach is ecological and evolutionary, and there is little direct discussion of physiology, except in so far as this comes into the relations between parasites and their hosts. In short, this is largely a consideration of the natural geographical distribution of

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

parasites, and as such it is very welcome.

The translation is good in spite of some awkwardnesses of phraseology and mistakes in nomenclature. One striking example of such an error, repeated three times, is the reference to *Arion ater* as a nudibranch.

There are two bibliographies, one of Russian and one of non-Russian literature. The illustrations, all in black and white, are very good and numerous.

A. D. Hobson

COMPARATIVE ANATOMY

Dynamics in Metazoan Evolution: the Origin of the Coelom and Segments, *by R. B. Clark. Pp. x+313. Clarendon Press, Oxford: Oxford University Press, London 1964. 48s. net.*

This book would have delighted the hearts of zoologists at the beginning of the century when they were worried by questions relating to the origin and evolution of the coelomic cavity and of metameric segmentation, but were unable to answer them. The author approaches the problem by asking what conferred survival value on those forms in which a coelom and metamery had evolved. He provides answers by analysing the function in locomotion of the musculature of the body in non-coelomate, coelomate but unsegmented, and segmented animals. The importance of the coelom is that it provides a hydrostatic skeleton. Non-coelomate animals move on surfaces by ciliary action but cannot change their shape powerfully enough to perform external work. This is, however, possible in coelomates, which are thereby able to burrow and to exploit a new habitat.

The significance of metamery in invertebrates lies in the septa which make it possible for peristaltic waves passing down the body to perform powerful work. In chordates, the segmental muscles are exclusively used for undulatory swimming movements, and their segmentation was evolved independently.

This book should be of great interest to morphologists, physiologists, and all concerned with evolution. *Gavin de Beer*

THE BRAIN

A Model of the Brain, *by J. Z. Young. Pp. vii+348. Clarendon Press, Oxford: Oxford University Press, London 1964. 35s. net*

This book is based on the William Withering lectures given at the University of Birmingham. All readers will feel indebted to those who invited Professor Young to give the lectures, because the resulting volume is a very stimulating one and will be of great value to those of many disciplines who are interested in nervous mechanisms. The author discusses some of the general principles involved in the application of knowledge gained from computers and other physical systems as aids to our understanding of the brain. He emphasizes particularly its homeostatic function, and it is this role which gives a direct invitation to the bio-engineer to apply his knowledge. Anatomical, physiological, psychological, engineering, and philosophical concepts are integrated with great lucidity and presented with the enthusiasm which one associates with this author's books.

The main part of the book is concerned with the model itself, and is based on the octopus brain. Most of the research on the octopus brain is based on its functional anatomy and on experiments using whole animals in conditioning and other learning situations. At the same time this work is united with knowledge of the mammalian brain, and this results in a most convincing and readable description of the present state of knowledge in this important field of research.

G. M. Hughes

GERONTOLOGY

Advances in Gerontological Research, *Vol. I, edited by B. L. Strehler. Pp. xi+410. Academic Press, New York and London. 1964. 96s. 6d. net.*

This book contains eleven review articles on various aspects of the study of ageing, edited by B. L. Strehler, himself a contributor, and published to the usual high standards of Academic Press. The subjects covered include age pigments, their structure and distribution; changes in the metabolism and physical properties of proteins; changes in the cell nucleus and nucleic acids; and genetic factors associated with ageing. Many of the articles are disappointing recitals of recent, rather than current, advances in the subject, and it seemed to the reviewer that too much emphasis was laid on the subject of age pigments. The irregularity of the appearance of these pigments makes them unreliable as an index of ageing, and the irreversibility of their production makes them unsuitable as an experimental subject. There seemed, too, to be an unfortunate amount of speculation, very little conclusion, and still less experimentally verifiable hypothesis.

But for all their shortcomings, many articles, particularly those from Rumania and the Soviet Union, contain very stimulating passages. The publication as a whole is an excellent corrective to those workers in the field of ageing who tend to ignore every hypothesis but their own.

Colin Muir

LIPID RESEARCH

Advances in Lipid Research, *edited by Rodolfo Paoletti and David Kritchevsky. Vol. I, pp. xii+418, 1963, 100s. net; Vol. II, pp. xi+499, 1964, 114s. 6d. net. Academic Press, New York and London.*

Many significant advances have been made in lipid research within the last two decades, and the importance of lipids is now recognized in many biological fields. Lipid research continues to expand very rapidly, and this new series of 'Advances' has been introduced to aid cross-fertilization within the broad area of lipid research.

Volumes I and II together contain eighteen articles. There are critical reviews on two new areas of research which promise to be stimulating and profitable, the plant sulpholipid (Benson), and the phosphatidylglycerols and lipoamino acids (Macfarlane). There is an excellent article on the physical structure and behaviour of lipids (Bangham), which includes a discussion of the importance of lipid structures in biological materials. Other chapters covering aspects of lipid structure, function, metabolism, biosynthesis, synthesis, and composition provide a wealth of specialized information.

The quality of the articles is generally high, but the editors might have given more thought to the planning of each volume. One article in Vol. II duplicates much of one in Vol. I, and one-quarter of the total subject matter (three articles) is devoted to aspects of atherosclerosis. This seems an excessive coverage of a subject which is regularly reviewed in its own journal. *G. M. Gray*

BACTERIAL ENDOTOXINS

Bacterial Endotoxins, *edited by Maurice Landy and Werner Braun. Pp. xvi+691. Institute of Microbiology, Rutgers, New Jersey. 1964. $12.*

Bacterial endotoxins are components of bacteria of interest both in microbiology—because of their importance to the bacterium, for instance as a component of its cell-wall or envelope—and in medicine and physiology—because of the profound and diverse effects on mammals which result from injection of even minute amounts of these substances. This volume contains papers given at a Symposium at Rutgers University in September 1963, attended by most of the leading workers in the field. The inclusion, in

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

edited form, of the record of the discussions provides some welcome variety between the blocks of papers. Most of the fifty-odd contributions concern the interaction of endotoxin and animal—alteration of resistance to infection, immunological phenomena, tolerance and hyper-reactivity, and mode of action. A few contributors describe recent advances in our knowledge of the structure of these large and complex molecules. The book is well produced and should prove most valuable. *B. A. D. Stocker*

FUNGI

Thermophilic Fungi, an Account of their Biology, Activities, and Classification, *by Donald G. Cooney and Ralph Emerson. Pp. xii+188. W. H. Freeman & Co., San Francisco and London. 1964. 36s. net.*

This excellent book gives a comprehensive yet detailed account of a very specialized group of fungi—the thermophiles. They are defined as those species which will grow at or above 50°C but which will not grow at 20°C. Thirteen species satisfy these rigorous requirements, and all of them have been studied in culture by the authors. Methods of isolation and culture are described in the opening chapters. This is followed by individual discussions of each recognized species. Full diagnoses are given for each species, their taxonomy is discussed, and full details of their temperature relations are recorded. The book concludes with three chapters on the general biology and practical importance of the thermophiles and a stimulating chapter on their remarkable physiological characteristics. It must now be considered essential reading for anyone interested in any high-temperature fermentation process, whether natural or industrial, but it will undoubtedly be read with pleasure by many others for its sheer intrinsic interest. The book is attractively produced at a reasonable price. *P. W. Brian*

POLLEN

Pollen Physiology and Fertilization, *edited by H. F. Linskens. Pp. xii+257. North-Holland Publishing Co., Amsterdam. 1964. 80s. net.*

There is considerable variation in the weight of experimental data in this account of the first international symposium on the subject, and in the significance of the subject matter in the different papers. There are a number of exciting electron micrographs, particularly in connection with pollen penetration and incompatibility, but even these clear pictures of cellulose fine structure after the removal of pectic substances leave one wishing for more convincing evidence that the pollen tube does actually grow between the cellulose micelles merely by secreting enzymes to dissolve pectic substances.

Biochemistry is somewhat scantily represented in this series and is not always free from the errors of a bygone era. The abnormally high proline content of pollen receives considerable attention, and one or two papers are in the highest tradition of biochemical investigation, with fascinating and puzzling evidence from tracer carbon studies of amino acid interconversions.

The biological aspect of the subject is represented by a lively discussion about the contribution of pollen tubes which enter the ovule too late to accomplish the act of double fertilization. Prof. Maheshwari's account of growth up to germination of seeds developed in test tube cultures from ovules scraped off the placenta into the tubes and mixed there with pollen is outstanding.

This book is something which no botanist, whether physiologist, biochemist, ecologist, or taxonomist, should miss reading. *S. E. Arney*

SPIDERS

Arachnida, *by Theodore Savory. Pp. viii+291. Academic Press, London and New York. 1964. 60s. net.*

The author is a well-known and devoted arachnologist. His book is divided into three main sections: one on the structure and physiology, embryology and growth, behaviour and ecology, phylogeny, and classification of arachnids in general; one on the structure (mainly external), distribution, taxonomy, and palaeontology of the separate orders; and one on miscellaneous topics such as economic arachnology, arachnid venom, spider webs, arachnids in amber, arachnophobia, and historical arachnology.

The book will give the student a broad introduction to the arachnids, particularly in respect of their classification, distribution, and external features (illustrated with admirably clear line drawings). On the experimental and physiological side there are a number of errors and omissions. For example, chitin is not 'a polypeptide, belonging to the sclero-protein group' and is not synonymous with cuticle; lyriform organs are mechano-receptors analogous to the campaniform sensillae of insects; it is not necessary for a newly moulted spider to exercise its legs to prevent the joints from hardening.

The standard of production is excellent and there are very few printer's errors, although figure 9 seems to have been printed upside down. *D. A. Parry*

HAGFISH

The Biology of Myxine, *edited by Al, Brodal and Ragnar Fänge. Pp. xiii+588. Oslo University Press; Dawsons, London. 1963. £6 net.*

Hagfish, like their fairly distant relatives the lampreys, are interesting as living clues to what the earliest vertebrates may have been like. They have been studied carefully by several of the foremost ichthyologists of the past and by others again more recently. It is very useful to have so much of the available information drawn together in this monograph, which has been published in honour of Professor Jan Jansen.

Twenty-four authors, from three continents, contribute twenty-eight articles, covering most aspects of the biology of myxinoids, dealing with all the main organ systems and including many details of the biochemistry, fine structure, histology, and physiology. Like so many journeys to the frontiers of knowledge, some contributions are rather dull and a few unduly discursive. One might also complain about the brevity of the index and the absence of cross-references; one example occurs when various authors reach different conclusions on the question as to whether the transition from earlier chordates to vertebrates is best regarded as having taken place in marine, brackish, or fresh water. But the general standards, of articles and editing alike, are very high, and the volume is beautifully produced and illustrated. Hagfish are more remote from fishes than the latter are from us, and they differ, too, from the images that many of us formed of them from the textbooks of our youth. *E. W. Knight-Jones*

THE LIVER

The Liver: Morphology, Biochemistry, Physiology, *edited by Ch. Rouiller. Vol. I, pp. xiii+683, 1963, $26; Vol. II, pp. xiv+674, 1964. 171s. 6d. net. Academic Press, New York and London.*

This treatise surveys in comprehensive form the entire field of present knowledge of the liver in normal and pathological conditions, as revealed by morphological and physiological studies; these studies are often based on modern methods of investigation, such as electron microscopy, isotope labelling, histochemistry, and cytochemistry. It is a valuable work of reference that bridges the gap between studies of the minutiae

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

of the structure and function of the liver, and more general works on human pathology.

Volume I deals with the embryology and morphology (macroscopic, microscopic, and ultramicroscopic) of the liver, with its biochemical functions (the metabolism of proteins, lipids, and carbohydrates). Volume II considers the excretory function of the liver cells; the Kupffer cells; and the relationship between the functions of the liver and the endocrines, vitamins, and blood, including liver function tests, methods of experimental surgery, and experimental pathology.

Here is much valuable information, which cannot otherwise be found except by close searching through the original literature. References and indexing are comprehensive. *Alan H. Hunt*

CANCER RESEARCH

Advances in Cancer Research, *Vol. VIII, edited by Alexander Haddow and Sidney Weinhouse. Pp. viii+482. Academic Press, New York and London. 1964. 121s. 6d. net.*

Because of the multiplicity of scientific disciplines now contributing to cancer research, the appearance of a new volume of 'Advances' is always welcome. More than half the present volume is devoted to two aspects of chemical carcinogenesis of practical consequence. The more comprehensive review deals with biological and chemical studies in experimental tobacco carcinogenesis and with the reduction of the tumorigenicity and cilia-toxicity of cigarette smoke. The role of contaminated foodstuffs as an environmental carcinogenic hazard has only recently been recognized; an assessment of current knowledge and its broad implications in modern food processing is therefore especially timely. A stimulating feature of both reviews is the particularization of the numerous unexplored problems.

Three further chapters present cogent appraisals of the structure of tumour viruses, nuclear proteins of neoplastic cells, and nucleolar chromosomes. Since nuclear protein chemistry is still in its infancy, much of the treatment of this topic is concerned with experimental procedures; clear evidence for the function of nuclear proteins is not yet available. Nucleolar chromosomes are considered with reference to nucleolar organizers, to the origin of nucleolar substance, and to the role of the nucleolus in transmitting genetic information. The high standard of previous volumes is fully maintained in the current volume. *M. W. Partridge*

NUTRITION

Comparative Nutrition of Man and Domestic Animals, *by H. H. Mitchell. Vol. I, pp. xxi+701, 1962, 178s. 6d. net; Vol. II, pp. xxi+840, 1964, 200s. net. Academic Press, New York and London.*

This two-volume work correlates the nutrient requirements of man and his domesticated animals, and the factors that modify these requirements. Much emphasis is given to background information concerning the various nutrients, their function and their inter-relationships in the body. The subject matter is arranged so that the net requirements may be converted into practical terms, and the book will interest those concerned with feeding man and farm animals, as well as those studying the academic aspects of the subject.

Nutrition is still a new academic subject, and books of this calibre demonstrate the need to study it not as part of other subjects, but as a discipline in its own right. For example, the work on human obesity is here set beside that on fattening livestock, and the section dealing with the factors affecting the net availability of metabolizable energy begins with a consideration of the thermodynamics of the Krebs cycle and continues with a study of the wastage of nutrients and how this would affect feeding standards and our ideas concerning specific dynamic action.

In the final chapter, 'Fulfilment', the author allows himself some speculation about future trends and gives his assessment of the present state of knowledge. Perhaps the only disappointment is the sad defence of teleology in the finale, but this does not detract from what must be regarded as a major work by a leading authority who has contributed much by his own researches to our knowledge of human and animal nutrition.

D. S. Miller

PHARMACOLOGY

Evaluation of Drug Activities: Pharmacometrics, *edited by D. R. Laurence and A. L. Bacharach. Academic Press, London and New York. 1964. 900 pages in 2 vols.: Vol. I, 95s. net; Vol. II, 90s. net.*

This book has 56 contributors. Its object is to provide reviews of the pharmacological methods used in the search for new drugs. For those engaged in this work these volumes will be valuable, because they cover so many different kinds of agents and give an authoritative account of the background knowledge. Included are antitumour agents, hypoglycaemic agents, blood cholesterol depressants, coagulants, iron-containing haematinics, diuretics, antihypertensive agents, active polypeptides, adrenocorticoid activity, brain-stem depressants, and antithyroid agents, as well as many others.

Since each author is a specialist in the field he covers, these volumes may do much to raise the standard of the work carried out in many laboratories and to broaden the minds of those who work in a limited area.

It is inevitable that many points of a method cannot be properly described by the written word, and it might have helped if the editors had taken it upon themselves to stress the great value of a personal visit to the expert. Perhaps the most important precept of all is that the beginner will save much time and money by seeing the method in use by an experienced man. However, the editors are to be congratulated on completing this large task. *J. H. Burn*

GLASS-CERAMICS

Glass-Ceramics, *by P. W. McMillan. Pp. viii+229. Academic Press, London and New York. 1964. 47s. 6d. net.*

Glass-ceramics are polycrystalline solids prepared by the controlled crystallization of glasses, and the ease with which crystals can be precipitated from a glass-forming liquid can be controlled by variation of composition and heat treatment. In liquids in which crystallization is difficult, the two stages of nucleation and crystal growth can be studied separately. Glass-ceramics are obtained by producing very large numbers of nuclei so that the final crystals are very small. Suitable compositions lead to strong materials and, if desired, to materials with zero or negative thermal expansion.

This book provides an excellent summary of the present position in this rapidly developing field, with particular emphasis on methods of producing useful materials. Immiscibility in the liquid phase and the phenomena of spinodal decomposition are not stressed as much as their importance would appear to demand.

The first three chapters discuss the history of glass-ceramics, the mechanism of the precipitation of crystals from glasses and the more recent work on nucleation and crystal growth. The preparation of glass-ceramics and their properties and applications are described in the remaining four chapters.

R. W. Douglas

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

METALLURGY

The Theory of Order-Disorder in Alloys, *by M. A. Krivoglaz and A. Smirnov. (Translated from the Russian by Scripta Technica, and edited by Bruce Chalmers.) Pp. x+427. Macdonald & Co. (Publishers) Ltd, London. 1964. 90s. net.*

Tammann postulated in 1919 the possibility of ordering in alloys, and his predictions were confirmed in the next decade, but it was not until the 1930s that extensive study of ordering was undertaken and the principal experimental and theoretical features were expounded. Interest revived after the war, particularly in Russia. The detailed study of the theory of order-disorder transformations was pursued there, partly for its own sake but also as part of the general study of the solid state. The authors of this book played a prominent part in this study.

They review in the first quarter of the book the experimental results that are necessary for illustration of the theoretical studies which follow. Chapters II and III are devoted to thermodynamic and statistical theories of the ordering of alloys. A chapter on diffusion comes next, followed by a discussion of the motion of electrons in ordered crystals. Chapter VI is concerned with the scattering of X-rays and slow neutrons, and the two remaining chapters deal with the electrical, magnetic, optical, and mechanical properties of ordered alloys.

The authors have reviewed all the important theoretical studies of ordering phenomena and have produced a book of a high standard. It can be recommended to advanced workers in the fields of solid-state physics and physical metallurgy as well as to those whose main interest is in order-disorder transformations. *E. C. Ellwood*

GOLD

Gold; Recovery, Properties, and Applications, *edited by Edmund M. Wise. Pp. x+367. D. Van Nostrand Co. Inc., Princeton, New Jersey. 1964. 93s. net.*

In comparison with the enormous output required as backing for international currencies and other allied forms of bullion, the amount of gold finding its way into industrial or technical channels is small indeed. None the less, there is a steady increase in a number of such applications, many of them of a somewhat specialized nature.

The literature on the metallurgy of gold, probably for these reasons, has been sparse and any compilation of the available data on the properties and uses of this metal and its alloys is bound to be useful. The present work goes beyond this modest aim, and forms a most comprehensive survey covering all aspects of the extraction, refining, working, and general technology of gold. The chemical and physical properties of the metal are fully documented; a long section deals with all the known binary alloy systems and a few commercially important ternary systems; electro-deposition, dental alloys, carat golds for jewellery, and electrical and electronic applications are all adequately discussed. The analytical chemistry and metallography of gold are also included, as well as a chapter on the determination of trace impurities by spectrographic methods. Some twenty authors—all acknowledged authorities in their fields—have contributed to the volume, which will provide a most reliable work of reference. *L. B. Hunt*

HISTORY OF SCIENCE

The History of the Study of Landforms *or* **The Development of Geomorphology,** *Vol. I,* **Geomorphology before Davis,** *by Richard J. Chorley, Antony J. Dunn, and Robert P. Beckinsale. Pp. xvi+678. London: Methuen & Co. Ltd; New York: John Wiley & Sons Inc. 1964. 84s. net.*

This history of landform study considers the development of geomorphology before the first major statement by W. M. Davis in 1889 of the Cycle of Erosion.

Each of the four parts into which the volume is divided chronologically has its own list of references and a separate chapter or chapters on quantitative geomorphology. There are numerous illustrations—of early workers, of landscapes as drawn or photographed by them, and of landscapes argued about in the past and here portrayed in generally splendid air photographs. There is also an 'informative index', which includes geomorphologists and historians of science. Here as elsewhere there are succinct, indeed at times caustic, comments on the role played by individuals in the development of the subject.

Lengthy quotations are linked by brief summaries, shrewd comments, and biographical details. Even without referring to original sources, it is possible to obtain a reasonable idea of the major contributions of individuals and to assess the judgments passed on them by Chorley and his colleagues.

The overwhelming impression from this history is of the failure of geomorphology to advance on a rigorous quantitative basis. This volume will certainly aid immeasurably in the constant reappraisal of earlier ideas and indicate lines for future developments. It is in itself an outstanding contribution to the study of landforms. *V. B. Proudfoot*

HISTORY OF TECHNOLOGY

Britain and Atomic Energy 1939–1945, *by Margaret Gowing. Pp. xvi+464. London: Macmillan & Co. Ltd; New York: St Martin's Press. 1964. 55s. net.*

One often comes across a dull novel hiding behind an enticing title, so it is a welcome change to pick up a book with a matter-of-fact title like this one and find oneself uttering the hackneyed phrase 'I could not put it down.' Scholarly depth and historical insight may be taken for granted in Margaret Gowing, the Historian of the U.K. Atomic Energy Authority, but it is exhilarating to receive as a bonus such a mastery of style and presentation. The author has succeeded in weaving the many threads of her story into a tapestry equally satisfying in its broad outlines and in its vivid details.

The first part of the book takes us from the famous Frisch-Peierls Memorandum on the feasibility of a uranium 'superbomb', written early in 1940, to the summer of 1941, culminating in the Report of the Maud Committee. Both these documents have at last shed their 'secret' cloaks; they appear as appendices to the book and make interesting reading. The second part, fittingly entitled 'The Doldrums', describes the vacillations and Anglo-American suspicions and misunderstandings of the next two years and is in melancholy contrast with the purposeful and jaunty enthusiasm of the previous period. Finally the third part, 'The Exodus to North America' shows Britain and Canada in junior partnership with the U.S. and gives penetrating analyses of the political implications and of the use of the bomb. But on this last topic I missed the comments of H. L. Stimson, the then U.S. Secretary of War. To judge by his memoirs, the short time interval between the dropping of the Hiroshima bomb and that of the Nagasaki bomb was intended as a strategic bluff, since 'The two atomic bombs we had dropped were the only ones we had ready...' but '... so far as the Japanese could know, our ability to execute atomic attacks ... was unlimited.'

Mrs Gowing has written a profound and brilliant study about an intriguing phase and facet of modern history. Let us hope that she will give us, before long, the sequel to the story. *N. Kurti*

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Some books received

Digitized by Arya Samaj Foundation Chennai and eGangotri

07823

(*Note.* Mention of a book on this page does not preclude subsequent review.)

GENERAL SCIENCE

Frédéric Joliot-Curie: the Man and his Theories, *by P. Biquard. (Translated from the French by G. Strachan.) Pp. 224. Souvenir Press Ltd, London. 1965. 25s.*

Louis Pasteur. The Man and his Theories, *by Hilaire Cuny. (Translated from the French by Patrick Evans.) Pp. 190. Souvenir Press Ltd, London. 1965. 21s.*

The Philosophy of Science. A Systematic Account, *by Peter Caws. Pp. xii+354. D. Van Nostrand Co. Ltd, London. 1965. 52s. 6d.*

Tizard, *by R. W. Clark. Pp. xiii+458. Methuen & Co. Ltd, London. 1965. 50s. net.*

PHYSICS

Collision Phenomena in Ionized Gases, *by E. W. McDaniel. Pp. xxii+775. John Wiley & Sons Inc., London and New York. 1964. 132s.*

La détection des radiations infrarouges et ses applications, *by A. Dauguet. Pp. xiii+331. Dunod, Paris. 1964. Cloth, 72 Frs.*

The Discovery of Radioactivity and Transmutation. *Edited by A. Romer. Pp. xi+233. Constable & Co. Ltd, London; Dover Publications Inc., New York. 1964. 13s. 6d.; $1.65.*

Elementary Dynamics of Particles, *by H. W. Harkness. Pp. ix+219. Academic Press Inc., New York and London. 1964. Cloth, 48s.; paper, 24s.*

The Equilibrium Theory of Classical Fluids, *by H. L. Frisch and J. L. Lebowitz. Pp. xiii+Section I: pp. 1+77; Section II: pp. 1+323; Section III: 1+103. W. A. Benjamin Inc., New York and Amsterdam. 1964. Cloth, $11; paper, $6.55.*

Exploding Wires, *Vol. III. Edited by W. G. Chace and H. K. Moore. Pp. ix+410. 1964. Plenum Press, New York. 1964. $17.50.*

Heat, *by M. Nelkon. Pp. 324. (Second edition.) Blackie & Son Ltd, London and Glasgow. 1964. 18s.*

Heat and Thermodynamics, *by F. Tyler. Pp. viii+424. (Second edition.) Edward Arnold (Publishers) Ltd, London. 1965. 21s. net.*

Pressure Measurement in Vacuum Systems, *by J. H. Leck. Pp. xii+221. (Second edition.) Published on behalf of the Institute of Physics and the Physical Society. Chapman and Hall Ltd, London. 1964. 45s.*

Space-Age Acronyms – Abbreviations and Designations, *by Reta C. Moser. Pp. 427. Plenum Press, New York. 1964. $17.50.*

Theory of Superconductivity, *by J. R. Schrieffer. Pp. xiii+282. W. A. Benjamin Inc., New York and Amsterdam. 1964. $11.*

Unified Theory of Nuclear Models, *by G. E. Brown. Pp. viii+178. North-Holland Publishing Company, Amsterdam. 1964. 40s.*

Variational Techniques in Electromagnetism, *by L. Cairo and T. Kahan. Pp. xv+152. Blackie & Son Ltd, London and Glasgow. 1965. 27s. 6d. net.*

CHEMISTRY

Analysis of Ancient Metals, *by Earle R. Caley. Edited by R. Belcher and L. Gordon. Pp. xi+173. Pergamon Press Ltd, Oxford. 1964. 70s. net.*

Chemistry and Beyond. A Selection from the Writings of the late Professor F. A. Paneth. *Edited by H. Dingle and G. R. Martin; assisted by E. Paneth. Pp. xxi+285. John Wiley & Sons Inc., London and New York. 1964. 45s.*

Chemistry for Engineers – An Introductory Course, *by E. Cartmell. Pp. ix+172. (Second edition.) Butterworth & Co. (Publishers) Ltd, London. 1964. 27s. 6d. net.*

Coordination Chemistry – The Chemistry of Metal Complexes, *by Fred Basolo and Ronald Johnson. Pp. xii+180. W. A. Benjamin Inc., New York and Amsterdam. 1964. Cloth, $4.35; paper, $2.15.*

The Determination of Sterols: *The Society for Analytical Chemistry Monograph No. 2. Pp. iv+72. The Society for Analytical Chemistry, London. 1964. 15s.; $2.*

EDTA Titrations. An Introduction to Theory and Practice, *by H. A. Flaschka. Pp. 144. Pergamon Press Ltd, Oxford. 1964. 42s. net.*

Manuel pratique de chromatographie en phase gazeuse. *Edited by J. Tranchant. Pp. 231. Masson et Cie, Paris. 1964. 36 Frs.*

Peroxidase. The Properties and Uses of a Versatile Enzyme and of some Related Catalysts, by B. C. Saunders, A. G. Holmes-Siedle, and B. P. Stark. *Pp. x+271. Butterworth & Co. (Publishers) Ltd, London. 1964. 60s. net.*

Preparative Inorganic Reactions, *Vol. I. Edited by W. L. Jolly. Pp. ix+271. John Wiley & Sons Inc., London and New York. 1964. 68s.*

Progress in Boron Chemistry, *Vol. I. Edited by H. Steinberg and A. L. McCloskey. Pp. vii+487. Pergamon Press Ltd, Oxford. 1964. £7 net.*

Radiation Chemistry. *Edited by J. Dobó and G. V. Putirskaya. (Translated by the editors, T. Szávoszt, and I. Székely.) Pp. 482. Akadémiai Kladó, Publishing House of the Hungarian Academy of Sciences, Budapest. 1964. $14.*

Silicate Science, *Vol. II:* Glasses, Enamels, Slags, *by W. Eitel. Pp. xii+707. Academic Press Inc., New York and London. 1965. 186s.; subs., 164s. 6d.*

Solid State Charged Particle Detectors, *by Niels J. Hansen.* Progress in Nuclear Energy, *Series IX.* Analytical Chemistry, *Vol. IV, Part I. Pergamon Press Ltd, Oxford. 1964. 30s. net.*

Understanding Physical Chemistry, *by A. W. Adamson. Pp. xix+489. W. A. Benjamin Inc., New York and Amsterdam. 1964. Cloth, $11; paper, $4,34.*

Water and Solute-water Interactions, *by J. Lee Kavanau. Pp. 101. Holden-Day Inc., San Francisco, London, and Amsterdam. 1964. $5.50.*

Zonenschmelzen, *by H. Schildknecht. Pp. xii+226. Verlag Chemie, GmbH, Weinheim/Bergstr. 1964. 26 DM.*

METEOROLOGY

The Structure of Atmospheric Turbulence, *by J. L. Lumley and H. A. Panofsky. Pp. xi+239. John Wiley & Sons Inc., London and New York. 1964. 72s.*

BIOLOGY

Comparaisons multiples en biologie. Quelques problèmes courants et perspectives nouvelles, *by J. Th. Matsakis. Pp. 201. Centre National de la Recherche Scientifique. 1963. 14 Frs.*

Culture and the Direction of Human Evolution. *A symposium arranged and edited by S. M. Garn. Pp. 98. Wayne State University Press, Detroit. 1964. $4.95.*

Ontogenese und funktionelle Morphologie des Auges des Finnwals. Suppl. 50=1 ad Vol. 57, Acta Anatomica 1964, *by G. Pillerl and A. Wandeler. Pp. 74. S. Karger AG, Basle and New York. 1964. 20 DM.*

Glossaire de biologie animale, *by R. Husson. Pp. 280. Gauthier-Villars, Paris. 1964. 28 Frs.*

Techniques in Experimental Virology. Edited by R. J. C. Harris. *Pp. xiii+450. Academic Press Inc. (London) Ltd, London. 1964. 100s.*

BIOCHEMISTRY

Fluorescent Protein Tracing. Edited by R. C. Nairn. *Pp. xv+335. (Second edition.) E. & S. Livingstone Ltd, Edinburgh and London. 1964. 45s. net.*

An Introduction to the Chemistry of Carbohydrates, *by R. D. Guthrie and J. Honeyman. Pp. 144. (Second edition.) Clarendon Press: Oxford University Press, London. 1964. 21s. net.*

An Introduction to Physical Biochemistry, *by H. B. Bull. Pp. xii+433. Blackwell Scientific Publications Ltd, Oxford; F. A. Davis Company, Philadelphia, Pa. 1964. 68s.*

Nucleotides and Coenzymes, *by D. W. Hutchinson. Pp. viii+136. Methuen & Co. Ltd, London; John Wiley & Sons Inc., New York. 1964. 18s. net.*

Tetrapyrrole Biosynthesis and its Regulation, *by June Lascelles. W. A. Benjamin Inc., New York and Amsterdam. 1964. $7.70.*

Les triterpénoïdes en physiologie végétale et animale, *by P. Boiteau, B. Pasich, and A. R. Ratsimamanga. Pp. xi+1370. Published under the auspices of the Centre National de la Recherche Scientifique. Gauthier-Villars, Paris. 1964. 310 Frs.*

Vitamin B_{12}, *by E. Lester Smith. Pp. xii+180. (Third edition.) Methuen & Co. Ltd, London; John Wiley & Sons Inc., New York. 1965. 25s. net (U.K. only).*

BOTANY

Algae and Man. *Edited by D. F. Jackson. Pp. x+434. Plenum Press, New York. 1964. $14.50.*

Plant Metabolism, *by H. E. Street. Pp. ix+238. Pergamon Press Ltd, Oxford; The Macmillan Company, New York. 1963. 20s.*

Quantitative and Dynamic Ecology, *by K. A. Kershaw. Pp. viii+183. Edward Arnold (Publishers) Ltd, London. 1964. 30s. net.*

ZOOLOGY

Advances in Insect Physiology, *Vol. II. Edited by J. W. L. Beament, J. E. Treherne, and V. B. Wigglesworth. Pp. xi+364. Academic Press Inc. (London) Ltd, London. 1964. 70s.*

Animal Communication, by H. and M. Frings. *Pp. viii+204. Blaisdell Publishing Co., New York, Toronto, and London. 1964. Paper, $2.50.*

Bird Structure. An Approach through Evolution, Development and Function in the Fowl, *by D. A. Ede. Pp. 120. Hutchinson Educational Ltd, London. 1964. 15s.*

Dictionary of Herpetology, *by J. A. Peters. Pp. vii+392. Hafner Publishing Co. Inc., New York and London. 1964. $11.50.*

The Physiology of Insects, *Vol. I. Edited by M. Rockstein. Pp. xiv+640. Academic Press Inc., New York and London. 1964. 157s.*

PHARMACOLOGY

Advances in Drug Research, *Vol. I. Edited by N. J. Harper and A. B. Simmonds. Pp. x+209. Academic Press Inc. (London) Ltd, London. 1964. 50s.*

Steroid Drugs, *Vol. II:* Index of Biologically Active Steroids, *by N. Applezweig. Pp. ix+449. Holden-Day Inc., San Francisco, London and Amsterdam. 1964. $10.50.*

TECHNOLOGY

High-temperature Materials, *No. 3:* Thermal Radiative Properties, *by W. D. Wood, H. W. Deem, and C. F. Lucks. Pp. 470. Plenum Press, New York. 1964. $17.50.*

METALLURGY

Metallurgy at High Pressures and High Temperatures: *Edited by K. A. Gschneidner, Jr., M. T. Hepworth, and N. A. D. Parlee. Pp. xii+409. Gordon and Breach, Science Publishers Inc., New York. 1964. Cloth, $19.50; paper, $8.75.*

New Types of Metal Powders. *Edited by H. H. Hausner. Pp. ix+164. Gordon and Breach, Science Publishers Inc., New York. 1964. Cloth, $9.50; paper, $3.95.*

Made and printed in Great Britain at The Kynoch Press, Birmingham 6,
for the publishers, Imperial Chemical Industries Limited, Millbank, London S.W.1

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

Compiled 1999-2000

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

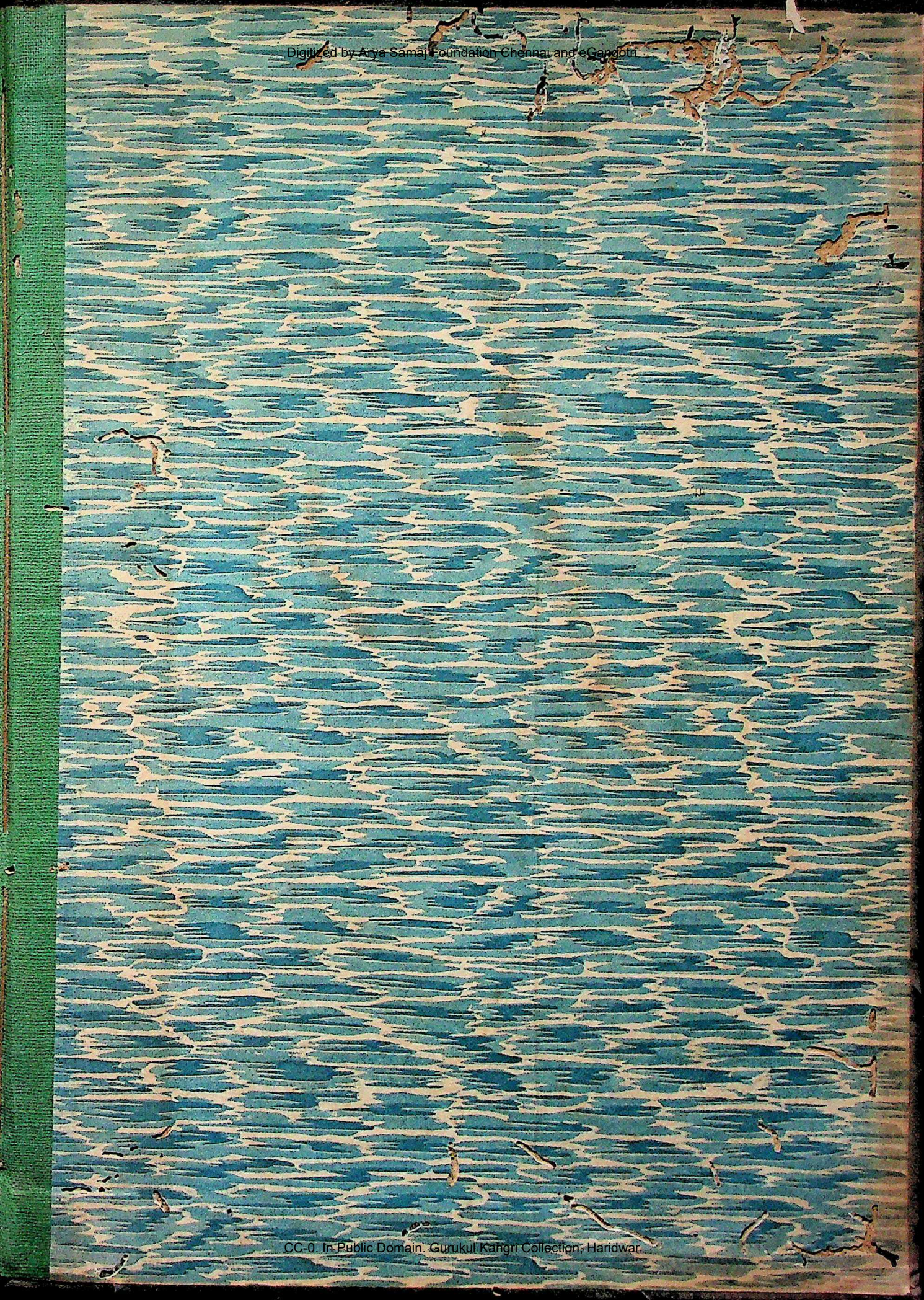
Digitized by Arya Samaj Foundation Chennai and eGangotri

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri

CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar

Digitized by Arya Samaj Foundation Chennai and eGangotri



CC-0. In Public Domain. Gurukul Kangri Collection, Haridwar